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PENETRATION THROUGH FACEPIECE RUBBER (U)

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Penetration Through Facepiece Rubber

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SUMMARY

This report starts out with a phenomenological description of the diffusion process clearly identifying the terminology involved as well as the methods used for measuring diffusion coefficients. The factors affecting diffusivities and the theories for predicting the dependence of diffusivity on concentration are also covered.

A comprehensive study of the effects of size and shape of several penetrants at different temperature levels is presented. Moreover, a study for the diffusion of battlefield contaminants; viz., gasoline, diesel fuel, aviation fuel, kerosene, trichloroethylene and bis(2-chloroethyl) sulphide in natural and bromobutyl rubbers is reported.

Changes to the current procedures followed by DREO for obtaining penetration data are proposed in this report. Such changes are essential for obtaining reliable and reproducible data.

A computer programme for calculating the theoretical concentration-time profile for the diffusion of bis(2-chloroethyl) sulphide in natural and bromobutyl rubber slabs is included in this report. This programme is based on a numerical solution of Fick's Second Law of diffusion for the case when the diffusion coefficient is dependent on concentration. The numerical solution was developed by Asfour et al. [1984].

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1. INTRODUCTION

1.1. General

The unique molecular structure of polymers distinguishes them from metal and glass. The long chain polymer molecules are not only versatile in their physical and mechanical properties, they also offer a new set of transport properties, somewhat in between conv ntional porous materials and hard metal and glasses.

The interest in diffusion of liquids, vapours and gases in polymers originates from an academic point of view, as well as from industrial needs. Industrial applications include polymer membrane separations, biomedical engineering devices, dyeing of textile fibers, surface coatings and using polymer films as resisting barriers under various hostile environments. Since the early seventies, the disclosure of toxicity of monomers, especially vinyl chloride monomer in the PVC industry,created an enormous interest in the subject. Some of these topics have been reviewed by a number of researchers, e.g., Li et al. [1965], Kesting [1971], Rembannes and Shen [1971], Hopfenberg [1974], Turbak [1981] and Gordan [1985]. The academic side of the subject includes polymer structure-diffusion properties relationships.

Diffusion is a process by which matter is transported from one

part of a system to another as a result of random molecular motions. This results in an equalization of concentration in the system and eventually produces an equilibrium state. Results of diffusion studies are usually reported in terms of diffusion coefficients which are rate constants.

The diffusion coefficient of organic molecules in polymers can be measured by a number of techniques, depending on the system under investigation. Among these the sorption/desorption technique is the most commonly used, since it is relatively more versatile than other techniques. For a polymer/organic system the diffusion coefficient is controlled by a number of factors such as the nature of the polymer and diffusant, concentration of the diffusant and temperature. The influence of these and other factors on diffusion coefficients can only be evaluated by conducting diffusion experiments under suitable conditions.

1.2 Statement of Work

The statement of work for this project includes:

(i) reviewing DREO procedures for obtaining penetration times and identifying changes in experimental procedures required to obtain material constants as well as protection times,

(ii) analyzing penetration data provided by DREO on bromobutyl and

natural rubber samples,

(iii) setting up an experimental apparatus and measuring the diffusion of organic molecules (including battlefield contaminants and bis(2-chloroethyl) sulfide in rubbers and plastics (including bromobutyl and and natural rubber),

(iv) (a) conducting diffusion measurements on bromobutyl and natural rubber with bis(2-chloroethyl) sulphide (at DREO) and from this data calculate the diffusion coefficients,

(b) using a mathematical model and the diffusion coefficients measured above, provide theoretical concentration/time profiles for the penetration of bis(2-chloroethyl) sulphide through slabs of 0.07" natural and bromobutyl rubber,

(v) conduct experiments to compare information obtained by absorption and penetration studies.

Consequently, in this report we will review DREO procedures and provide an analysis for the data provided by DREO.

As far as the third statement of work is concerned we have accomplished the following:

(i) a sorption /desorption apparatus was set up, which consists of an electronic microbalance, vacuum line and a microcomputer based monitoring equipment. All the experiments were performed on this equipment using the desorption technique,

(ii) the diffusion coefficients at zero penetrant concentration, D_o, of dichloromethane, chloroform, carbon tetrachloride cyclohexane, benzene, o-xylene, m-xylene, p-xylene and n--hexane in low density poly(ethylene) (LDPE) were measured at 25°C. The temperature dependence of diffusion coefficient of toluene and n-hexane in LDPE were also investigated in a limited temperature range of 25-45°C,

(iii) the D_o of relatively elongated and branched molecules of saturated hydrocarbons (n-hexane, n-heptane, n-octane, n-decane and trimethyl pentane) in LDPE were measured at 25, 35, 40, 45, and 50°C,

(iv) the precision of the method paved the way to investigate diffusion in vulcanized natural rubber films of various thicknesses. Diffusion of trichloroethylene, kerosene oil, gasoline, diesel fuel, and aviation fuel were investigated at 25°C,

(v) the D_o of trichloroethylene, kerosene oil, gasoline, and

aviation fuel in Bromobutyl rubber films were also measured at 25°C. Here also, films of various thicknesses were used.

Experiments were conducted at DREO on the diffusion of bis(2-chloroethyl) sulphide into bromobutyl and natural rubbers. These measurements were used to (i) calculate the pertinent diffusions coefficients, and (ii) provide theoretical concentration/time profiles as will be explained later in this report.

Finally, a comparison is made between the information obtained in this study and those provided by DREO.

The experimental data on diffusion of organic penetrants enabled us to correlate the size and shape effects of the penetrant with diffusion coefficient. Moreover, we were able to explain the temperature effect on diffusion coefficients in terms of activation energies.

The interpretation of diffusion data requires evaluation of some of the physical properties of the polymer, such as its glass transition temperature, crystallinity and the amount and nature of additives in the polymers. Similarly, the molar volume of the penetrant, its shape and solubility, etc. has to be known. Once this information is obtained then the diffusion phenomenon for the system under study can be explained on a theoretical basis. There are a number of theories concerning diffusion in polymers, however, the free

volume theory has the most acceptability. Generally, free volume is considered to be the free space in the system.

Having obtained the diffusion data and the related information about LDPE/penetrant systems, we explained the results in terms of the free volume theory and found that the results fitted the theory satisfactorily

Since no information was available on the composition of natural and bromobutyl rubber films, and neither did we know the exact composition of battlefield contaminants, viz., aviation fuel, gasoline, ... etc., it was therefore not possible to explain these results on a theoretical basis.

As a whole, we succeeded in establishing a relationship between the size and shape of the penetrants and their diffusion coefficients in LDPE, which will be helpful in studying this effect in other polymer films. We also could establish the effect of temperature on this relationship.

2. PHENOMENOLOGICAL DESCRIPTION OF THE DIFFUSION PROCESS

2.1. General

Diffusion is a process by which matter is transported from one part of a system to another. The driving force of diffusion is still a controversial matter. Concentration gradient has long been used as the driving force behind any diffusional process; however, developing the diffusion equation using arguments based on thermodynamics of irreversible processes suggests that the chemical potential gradient is the true driving force of diffusion. Experimental evidence confirming that chemical potential gradient is the driving force of diffusion has been obtained, e.g., Cullinan and Lenczk [1969]. However, Dankwerts [1971] argues that suggesting that using the gradient of chemical potential as a driving force of diffusion is inconsistent with the random nature of the process. Dullien [1979], indicated that Dankwerts' argument is equivalent to the proposition that the magnitude of the tendency for a non-ideal solution to reach equilibrium is simply proportional to the concentration gradients which is clearly in contradiction with experience as expressed in the basic principles of thermodynamics

Diffusion can be described by Fick's first law which is given by:

$$\vec{F}_A^{\,c} = -D_F \nabla C_A \qquad (2.1)$$

where $\vec{F}_A^{\,c}$ represents the flow of component A in moles per unit area per unit time with respect to fixed co-ordinates. C_A is the concentration of component A, in moles per unit volume and D_F is known as the "Fickian diffusivity" and has the dimensions of area per unit time.

When diffusion is considered to take place in one direction, i.e., there is a concentration gradient only along the x-axis, then Equation (2.1) can be rewritten as follows:

$$F_A = -D_F \frac{d C_A}{dx} \qquad (2.2)$$

Equations (2.1) and (2.2) are rigorous only in case of ideal systems, i.e., composition independent partial molar volumes. For systems showing a large volume change on mixing, the use of the aforementioned equations may result in significant errors in the value of the diffusion coefficients.

For cases where unsteady-state diffusion takes place, Fick's second law of diffusion may be used. Equation (2.3) gives Fick's second law for unidirectional diffusion.

$$\frac{\partial C_A}{\partial t} = D_F \frac{\partial^2 C_A}{\partial x^2} \qquad (2.3)$$

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In Equation (2.3), it was assumed that the diffusion coefficient does not depend on concentration. When the diffusion coefficient depends markedly on the concentration, then Equation (2.3) can be rewritten as follows:

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(D_F \frac{\partial C_A}{\partial x}\right) \qquad (2.4)$$

A complete definition of the diffusion coefficient, requires specifying both the units aand the frame of reference.

2.2. Terminology Used in Diffusion

2.2.1. The mutual diffusion coefficient, D^v

Considering the inter-diffusion of A and B in a closed system and assuming no net change of volume on mixing, one can write:

$$F_A = -D_A^v \frac{d\, c_A}{dx} \qquad (2.5)$$

$$F_B = -D_B^v \frac{d\, c_B}{dx} \qquad (2.7)$$

where c_A and c_B are the concentrations of A and B in mass units per unit volume of the mixture. The dimensions of D_A^v and D_B^v are area per unit time.

If the specific volumes of A and B are denoted by v_A and v_B, and if one envisages that A and B interdiffuse across a plane through which there is no net transfer of volume, then it follows from Equations (2.5) and (2.6) that:

$$v_A F_A = v_B F_B \tag{2.7}$$

or

$$v_A D_A^v \frac{d c_A}{dx} + v_B D_B^v \frac{d c_B}{dx} = 0 \tag{2.8}$$

Now, one can write:

$$v_A c_A + v_B c_B = 1 \tag{2.9}$$

which upon differentiation with respect to x, yields:

$$v_A \frac{d c_A}{dx} + v_B \frac{d c_B}{dx} = 0 \tag{2.10}$$

In order that Equations (2.8) and (2.10) be satisfied it follows that:

$$D_A^v \equiv D_B^v \tag{2.11}$$

Consequently, the behavior of a two component system,

satisfying the condition of no volume change on mixing, may be described in terms of a single diffusion coefficient, which may vary with composition. Such single diffusion coefficient is referred to as the mutual diffusion coefficient.

2.2.2. The intrinsic diffusion coefficient, $\mathcal{D}_i$

On the basis of his observations while studying diffusion in metal alloys, Darken [1949] argued that the use of diffusivities as commonly defined is inadequate for describing the diffusion phenomena. Darken [1949] proposed the use of two diffusivities in binary systems, one for each component.

Hartley and Crank [1949] extended Darken's treatment to liquid solutions. They assumed that due to the difference of the mass and size of two interdiffusing species A and B, a hydrostatic pressure tends to build up in the region of the solution which contributes least to the volume rate of transfer. This pressure is relieved by a compensating mass flow of A and B together, that is of the whole solution.

On that basis, Hartley and Crank [1949] argued that the overall rate of transfer of A across a volume fixed section may thus be expressed as the combined effect of a mass flow and a transfer due to pure diffusion. Since the amount of A transferred by the mass flow of the whole solution is proportional to the concentration of A, it

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follows that the diffusion coefficient D_A must necessarily be a function of the concentration of A. Consequently, Hartley and Crank [1949] argued that from the point of view of interpreting diffusion coefficients in terms of molecular motions, the mutual diffusion coefficient, D^V, thus appears to be unnecessarily complicated by the presence of mass flow. This prompted Hartley and Crank [1949] to define new diffusion coefficients; viz., $\mathfrak{D}_A$ and $\mathfrak{D}_B$ in terms of the rate of transfer of A and B, respectively, across a plane fixed so that no mass flow occurs through it.

Hartley and Crank [1949] provided the following relationship between the intrinsic diffusivities and mutual diffusivity:

$$D^V = V_A C_A(\mathfrak{D}_B - \mathfrak{D}_A) + \mathfrak{D}_A \qquad (2.12)$$

where C_A denotes the concentration of component A, and V_A is the constant volume used in the definition of concentration. If the molal volumes vary with composition, the coefficient D^V has no physical significance but $\mathfrak{D}_A$ and $\mathfrak{D}_B$ can still be defined in terms of the rates of transfer of A and B, respectively across a plane which moves so that there is no bulk flow of A and B together through it [Crank, 1979].

The foregoing discussion implies that there are two diffusion coefficients, one for each component, which in case of diffusion is not meaningful. This is because in diffusion, for a two-component

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system there is only one coefficient. However, Crank and Park [1968], indicated that, in several instances, diffusion measurements have been evaluated in terms of intrinsic diffusion coefficients.

When volume change on mixing accompany diffusion in a certain system, it is usual to select a suitable frame of reference so that the diffusion of component B with respect to that frame of reference is zero. This permits denoting the diffusivity of component A as D_A. Such diffusion coefficient can be related to the mutual diffusion coefficient by [Crank and Park, 1968]:

$$D_A^B = D^V \phi_B^2 \qquad (2.13)$$

where ϕ_B is the volume fraction of component B.

The value of D^V or D_A^B must be known in order to evaluate $\mathfrak{D}_A$ and $\mathfrak{D}_B$ separately.

For diffusion in solvent-polymer systems, the intrinsic diffusion coefficient for the polymer is very small compared with that of the solvent. In fact, the intrinsic diffusion coefficient of the polymer, $\mathfrak{D}_B$ can be assumed zero. Consequently, Equation (2.12) can be rewritten as follows:

$$D^V = \mathfrak{D}_A(1 - V_A C_A) = \mathfrak{D}_A \phi_B \qquad (2.14)$$

using Equation (2.13):

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$$D_A^B = \mathcal{D}_A \phi_B^3 \qquad (2.15)$$

where ϕ_B is the volume fraction of the polymer. In deriving Equation (2.15) it is assumed that diffusion takes place perpendicular to the polymer film. This may be a good assumption at the initial stages of sorption, however, at the latter stages relaxation stresses in the polymer film can cause expansion in the plane of the polymer film. Moreover, it is unlikely that swelling can be either strictly unidirectional or, isotropic. Consequently, Garret [1965] suggested the use of the following equation:

$$\mathcal{D}_A = \frac{D_A^B}{\phi_B^{7/3}} \qquad (2.16)$$

2.2.3. The thermodynamic diffusion coefficient, D^*

As indicated earlier, concentration gradient has long been used as the driving force behind any diffusional process. Developing the diffusion equation using irreversible thermodynamical arguments suggested using the chemical potential gradient as the driving force of diffusion rather than using the concentration gradient. Therefore, the mutual diffusion coefficient defined by Equations (2.5) and (2.6) should be corrected. It has been shown [e.g., Dullien, 1960] that usually:

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$$D_A^* = D_A^V/\beta' \qquad (2.17)$$

$$D_\beta^* = D_B^V/\beta' \qquad (2.18)$$

where

$$\beta' = \frac{d \ln a_i}{d \ln x_i}$$

where a_i and x_i are the activity and the mole fraction of component i, respectively. β' is generally called the thermodynamic correction factor.

Ghai et al. [1973], pointed out that the use of the thermodynamic correction factor, β', results in most of the cases, in "overcorrection" for the composition dependence of the diffusion coefficient. In other words, it changes a positive deviation from linear dependence of the diffusion coefficient on composition to a negative one, and vice-versa. In fact, it was shown for several systems, by Asfour [1979] and by Dullien and Asfour [1985] that ln D^* deviates from linearity more strongly and more often than ln D^V.

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3. REVIEW OF THE LITERATURE

3.1. General

In the previous chapter we presented a description of the diffusion process from a phenomenological standpoint and explained the terminology used in diffusion. In this chapter, we will review the experimental methods used in studying diffusion in polymers, the various sorption features, factors controlling diffusion of vapors and liquids in polymers and the existing theories for the interpretation of diffusion in polymers with emphasis on the free volume theory.

3.2. Methods for the Measurement of Diffusion Coefficients

Several methods are reported in the literature for the experimental study of diffusion in polymer films. A comprehensive review of these methods has been published by Crank [1979]. A brief account on each of these methods is in order.

3.2.1. Permeation methods

In these methods one surface of the polymer membrane is brought in contact with penetrant vapour at constant pressure. The other surface is kept at a lower vapour pressure. The quantity of the penetrant vapour permeating through the membrane is measured as a

function of time. The diffusion coefficient can be obtained from either of the two following methods:

(i) Steady state flux method

In this technique the flux, F, of the diffusing substance is obtained when one surface of the polymer membrane is kept at a fixed pressure p_1 and the other surface at a lower pressure p_2. At steady state:

$$F = -D\frac{dc}{dx} = \frac{D(C_1 - C_2)}{\ell} \qquad (3.1)$$

when the surface concentrations are not known, then

$$F = \frac{P(p_1 - p_2)}{\ell} \qquad (3.2)$$

where P is the permeability coefficient. D and P can be related to each other when the solubility is known:

$$D = \frac{P}{s} \qquad (3.3)$$

(ii) Time-lag method

If one surface of the polymer film is brought in contact with a gas or vapour at a fixed vapour pressure, some time is required before the penetrant appears on the evacuated side of the film. A quantitative measure of this time is related to the diffusion

coefficient by:

$$D = \frac{\ell^2}{6L} \qquad (3.4)$$

where ℓ is the thickness of the polymer film and L is the time-lag which is obtained by extrapolating the linear part of the pressure versus time curve of the steady state experiment.

3.2.2. Radiotracer method

This method provides useful information about the molecular mobility in diffusion without any overall gradient of chemical composition. If the diffusant is applied at the lower surface of the polymer film then the value of D can be calculated using the following equation:

$$\ln(A_\infty - A_t) = \text{const.} - \pi^2 Dt/\ell^2 \qquad (3.5)$$

where A_t is the β particle count at any time t and A_∞ is the β particle count after a time long enough to achieve uniform concentration of the diffusant throughout the polymer.

3.2.3. Determination of the concentration distance curves method

In this method the experimental problem consists of the determination of some concentration indicating physical properties as

a function of distance from an initially sharp boundary between the polymer and the penetrant. A refractive index technique has been developed by Crank and Robinson [1951], and a number of systems have been studied using this method. This technique has been applied subsequently by Hayes and Park, [1955] and Park and Said [1985].

This method requires a polymer sample, 1 mm thick, to be clamped between silvered optically flat glass plates and immersed in the liquid penetrant. The penetrant diffuses into the edge of the polymer sheet. The concentration differences produced result in the formation of Fabry-Perot fringes which are recorded by photomicrography and are used to calculate the concentration distance curves. It should, however, be pointed out that this method has not been widely used since the same data can be obtained by the simpler permeation methods.

3.2.4. Sorption kinetics

Various methods have been developed for measuring the uptake of penetrant vapours as a function of time. These methods begin with the direct weighing of the polymer sample after being exposed to vapours. Later on, a quartz spring was used and nowadays the electronic microbalance is being increasingly used.

Alternatively, the volume of the vapours sorbed can be measured directly. In some cases when sorption is fast, the

temperature of the polymer sample increases with time due to the heat of condensation of the vapours. Sorption may be controlled by the rate of loss of heat. A technique using air blasts, has been employed to overcome this difficulty.

A relationship between the diffusion coefficient and the initial rate of vapour sorption in a polymer can be obtained from Fick's second law of diffusion [Crank, 1979]:

$$D = \frac{\ell^2 \pi}{16} \left(\frac{M_t/M_\infty}{t^{1/2}} \right)^2 \qquad (3.6)$$

where D is the diffusion coefficient, ℓ is the thickness of the polymer sheet and M_t and M_∞ are the amount of vapour sorbed at time t and at equilibrium, respectively. The value of D can be deduced from the observation of the initial gradient on the graph of M_t/M_∞ versus $t^{1/2}$.

For a concentration dependent diffusion coefficient, the method of interval sorption is adopted where a series of sorption curves are produced for a range of concentrations. The initial gradients of each sorption curve yields a mean value of diffusion coefficient. Calculations have shown that for any one experiment D provides a reasonable approximation to:

$$\frac{1}{C_o} \int_o^{C_o} D \, dC \qquad (3.7)$$

By deducing values of D for each experiment and using the approximate relationship:

$$\bar{D} = \frac{1}{C_o} \int_o^{C_o} D \, dC \qquad (3.8)$$

a graph of DC_o as a function of C_o can be drawn and numerical or graphical differentiation with respect to C_o gives a first approximation to the relationship between D and C. In many cases this first approximation is sufficiently accurate. Alternatively, correction curves showing the difference between $1/C_o \int_o^{C_o} D \, dC$ and $\bar{D}/D_o$ can be used, thus avoiding the need for a second approximation [Crank, 1956]. Here, D_o is the value of D at zero penetrant concentration.

The method can be applied to combined sorption and desorption data. If D_s is calculated from the initial gradient for sorption and $\bar{D}_d$ from the gradient of desorption then $1/2(D_s + D_d)$ is a better approximation to $\frac{1}{C_o} \int_o^{C_o} D \, dC$ than either $\bar{D}_s$ or D_d.

During the later stages of diffusion the graph of $\ln(M_\infty - M_t)$

against time approaches a straight line whose slope is given by:

$$\frac{d}{dt}\left[\ln(M_t - M_\infty)\right] = -D_o \pi^2/\ell \qquad (3.9)$$

The final concentration during desorption tends to be zero. For constant D, both sorption and desorption experiments should yield the same value, otherwise sorption will yield $D(C_o)$ and desorption D_o.

3.3. Sorption Features

3.3.1. General

Polymers at temperatures above their glass transition temperature are in a rubbery state. At such a state polymers respond quickly to changes. Sorption in that case is known as "Fickian" sorption.

When a polymer is in a glassy state, i.e., below its glass transition temperature, the properties of such a polymer also tend to be time dependent. However, it should be noted here that in this case the time scale is quite different. Sorption and desorption of penetrant molecules result in structural changes as well as internal stresses which are believed to cause anomalous or non-Fickian behavior.

The following classification according to the relative rates of diffusion and polymer relaxation has been proposed by Alfrey et al.

[1966]:

(i) Fickian diffusion (known as Case I diffusion), in which the rate of diffusion is much lower than that of relaxation,

(ii) Case II diffusion, where diffusion is very rapid compared with the relaxation processes, and

(iii) non-Fickian or anomalous diffusion which occurs when the diffusion and relaxation rates are comparable.

A brief account of the characteristics of each of the above cases is in order.

(i) Fickian or Case I diffusion

When a plot of fractional uptake M_t/M_∞ versus $t^{1/2}$ is prepared, the following characteristics are observed in case of Fickian diffusion:

a. in the initial stages, the plot is linear,

b. when the relationship ceases to be linear, a curve concave towards the abscissa, is obtained,

c. when the diffusion coefficient increases with concentration, desorption is always slower than sorption

(ii) Case II diffusion

In some cases, it has been noticed that the sorption plots of weight gain versus time are linear [Alfrey et al. 1966 and Hopfenberg et al. 1969] and the transport is entirely controlled by the polymer relaxation and is known as Case II diffusion. It is characterized by

a sharp front moving into the polymer at constant velocity. This sharp boundary separates the outer swollen shell, essentially at equilibrium concentration, from an unpenetrated glassy core. Surface compression in the swollen gel will be balanced by the biaxial tension in the unpenetrated core of the specimen and a stress gradient is expected at the front. These internal stresses tend to extend the glassy core and increase the area of the sheet. It has also been suggested that solvent crazing and some form of stress crazing accompanies the Case II sorption process, provided sufficient large swelling stresses are generated at the boundary between the swollen polymer [Hopfenberg et al. 1970]. Recently, results of the internal stresses, generated during the swelling and the desorption process has been reported [Thomas and Windle 1981] and subsequently a theory has been proposed in terms of the diffusivity of the penetrant and the viscous flow rate of the polymer [Thomas and Windle 1982].

The kinetic parameters of the limiting relaxation and diffusion controlling mechanisms were obtained from the initial and final behaviour of liquid n-hexane sorption in glassy polystyrene [Nicholas and De Notaristefano 1984] and it has been reported that the overall solvent penetration process becomes diffusion controlled at high temperatures and at high values of the penetrant swollen shell.

(iii) Non-Fickian or anomalous diffusion

Crank [1979] indicated that if the amount sorbed at time t is denoted by $K t^n$, where K and n are constants, then Case I systems are

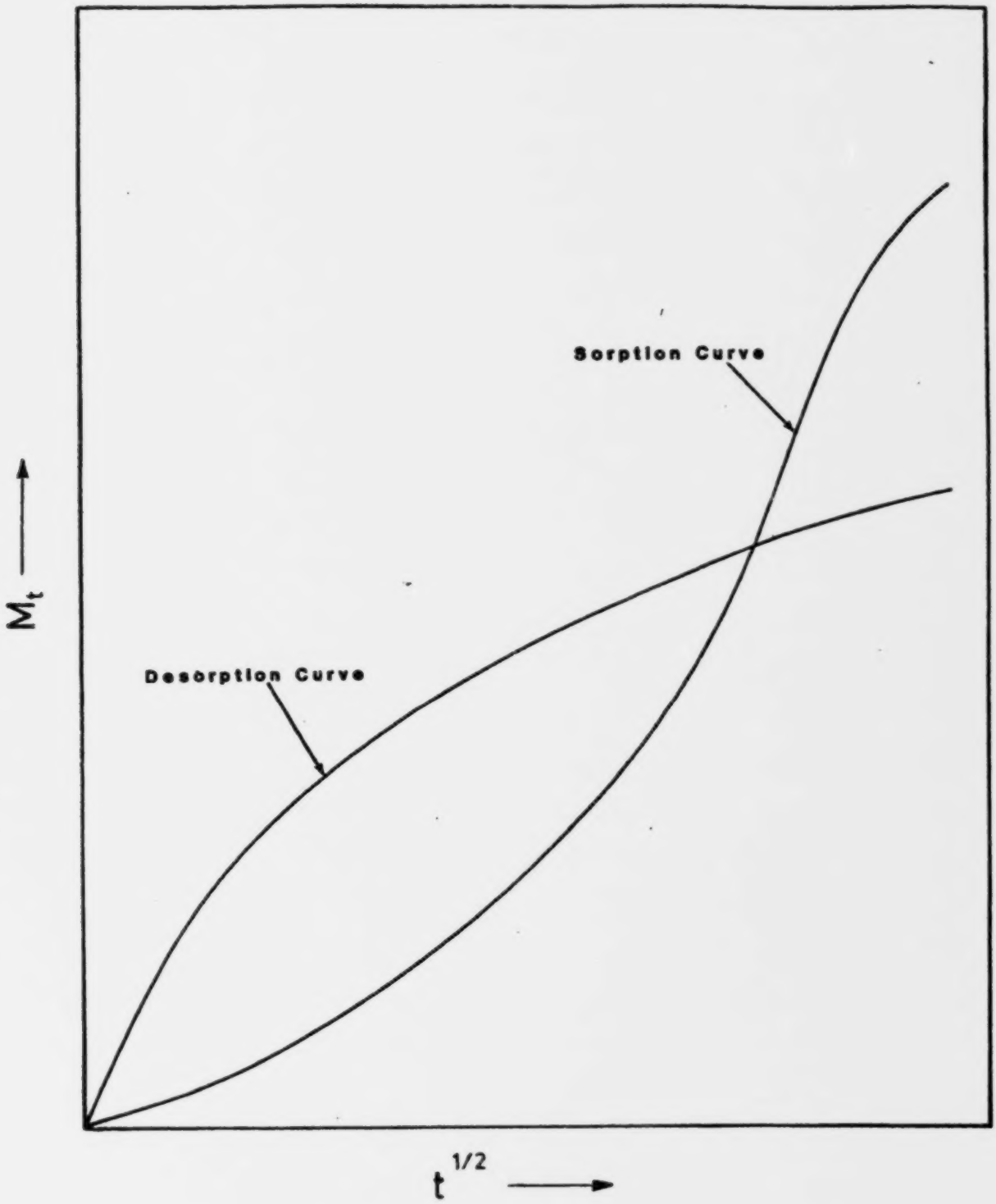

Figure 3.1- Sigmoid Curve

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characterized by n = 1/2 and Case II systems by n = 1. Non-Fickian systems lie between Case I and Case II, i.e., n takes a value between 1/2 and 1 or changes sigmoidally from one to the other.

Sigmoid curves of the shape of Figure 3.1 have been reported for many systems by Park [1968]. The sorption curves show a point of inflexion at about 50% sorption. Also, it appears from such curves that the initial rate of desorption exceeds that of sorption. However, the rate of desorption soon slows down and the curves cross.

3.4. Factors Affecting Diffusion of Vapours and Liquids in Polymers

The diffusion of vapours and liquids in polymers has features similar to those of gases, e.g., the temperature dependence, nature of the diffusant and the polymer are similar. However, due to the high solubility of vapours in polymers and the swelling of polymers, the changes in diffusion coefficients are quite different.

(i) Temperature

Diffusion in polymers is regarded as an activated process. The dependence of the diffusion coefficient can be expressed by an Arrhenius type relationship as follows:

$$D = D^{O} \, Exp[-E_d/RT] \qquad (3.10)$$

The relationship between ln D and 1/T has been reported to be linear

for many polymer penetrant systems, but it is only true for a limited temperature range and a decrease in E_d with increasing temperature has been observed for a number of systems. The dependence of E_d on T has been interpreted by a Transition State Theory, which predicts that the curved plots of E_d vs 1/T are due to the decrease in activation energy and activation entropy [Amerongen 1950]. It suggests that the energy required to create a hole of suitable size to accommodate the diffusing molecules, is almost the same as E_d. Alternatively, The Zone Theory assumes that the co-operative movement in several degrees of freedom is required in a zone of a polymer before a unit diffusion step can occur [Barrer 1957]. This suggests that the motion of several polymer segments is involved in the diffusion step.

Increasing the penetrant concentration also decreases the activation energy, E_d, values which can be related to the plasticization effect of the penetrant. Recently, the increase in diffusivity values with temperature has also been discussed under the Free Volume Theory [Duda et al. 1982].

(ii) <u>Diffusant</u>

Diffusion coefficients have been found to decrease with the increasing size of the penetrant molecule. For small molecules the decrease in diffusivity is accompanied by an increase in the activation energy of diffusion, but after a critical size has been reached, the activation energy no longer increases [Kokes and Long 1953]. This suggests that after this critical size, the unit step

involved in diffusion is the same as for the viscous flow situation. When the diffusing molecule is large its shape has a considerable effect on the diffusion rate. Studies on diffusion of n-hexadecane and DDT in plasticized PVC show that the larger but more flexible molecule of n-hexadecame diffuses more quickly than the smaller but rigid molecule of DDT [Park and Saleem 1984].

(iii) Nature of the polymer

a. Chemical structure

The free volume theory is based on the availability of local free volume in the polymer, which is related to the flexibility of the polymer chains and the cohesive energy of the polymer. It was found that due to its unsaturated backbone, polybutadiene had a higher diffusion coefficient than hydrogenated polybutadiene [Michaels aand Bixler 1961]. The introduction of methyl groups decreases the chain flexibility and results in a lower diffusivity value [Amerongen 1950]. Recent studies on the water-low density polyethylene system [McCall and Douglass 1984] suggest that solubility and diffusivity depend on the state of oxidation of the polymer. The oxygen groups act as traps to bind water molecules. Hydroxyl, hydroperoxide and carboxylic acid groups form the strongest traps. Ketones are weaker and ester groups exhibit negligible trapping.

b: Crosslinking

In some studies, it has been demonstrated that as the crosslinking increases, the diffusivity decreases and the activation

energy increases. Aitken and Barrer [1955], suggested that there is a tendency of the diffusion medium at high crosslinking to act as a molecular sieve. However, a smaller decrease for large molecules was also reported, which is contrary to the above mentioned claim [Mears 1957]. DeCandia et al. [1982] reported no change in diffusivity for crosslinked and uncrosslinked LDPE.

(iv) Glass transition temperature, T_g

In the study of sorption in polyvinyl alcohol [Mears 1957] it was noticed for the first time that the slope of the Arrhenius plot changes on passing through T_g. This was attributed to the increased segmental mobility of the polymer molecules above T_g. No changes were found in the slope of the Arrhenius-type plot for some gases [Stannet 1966] which indicate the possibility that some polymers have a mean hole size which leads to transition effects with large penetrant molecules only. For many polymer vapour systems the sorption is Fickian above the glass transition temperature. Also, it has been reported in many cases that the diffusivity increases with the lowering of the glass transition temperature [Saleem 1977], whereas non-Fickian sorption is observed below the glass transition temperature as explained earlier.

(v) Plasticizer

It is believed that the addition of a plasticizer decreases the cohesive forces between the polymer chains, thus resulting in an increase in the segmental mobility, which in turn results in an

increase in the rate of diffusion and a decrease in activation energy. A thorough study on the diffusion of various vapours in plasticized PVC confirms this behaviour [Saleem 1977]. It also reveals the effect of the chemical nature of the plasticizer on diffusion [Park and Saleem 1984].

It has also been observed in the diffusion of gases in polyvinyl chloride plasticized with tricresyl phosphate that the diffusion coefficient first decreased up to 15% concentration, i.e., it acted as an antiplasticizer by reducing the co-operative main chain molecular motion of polyvinyl chloride. However, beyond that limit of concentration the diffusivity was found to increase with increasing the concentration of the plasticizer [Sefcik et al. 1983].

(vi) Polymer morphology

The diffusivity of vapours in polymers is dependent on polymer morphology. In the case of polybutadiene, it was found that the diffusivity drops suddenly after a 75% trans content in the polymer. At this stage, there is an onset of crystallinity which increases from zero to 80% on moving from 75 to 100% trans content [Brown et al. 1973]. Studies on methylene chloride polyether ketone also show that the sorption of methylene chloride decreases with increasing crystallinity of the polymer [Stober et al. 1984], whereas the rate of desorption is found to be independent of crystallinity.

Thermal history, annealing, drawing and quenching of the

polymer also affect the sorption rates. Uniplanar oriented films show faster sorption [Drechsel et al. 1953]. Similar results were obtained for polystyrene samples with various draw ratios [Nicolais et al. 1979]. In the case of LDPE-toluene system it was observed that the diffusion behaviour of the oriented samples was non-Fickian [Bischoff and Eyerer 1984]. Annealing of these samples resulted in a decay of the orientation of the molecules and consequently a change in the diffusion mechanism. Also, annealing reduces the strain of the molecules and consequently, their influence is reduced. It is interesting to note that it has been suggested that the transport properties appear to be extremely sensitive probes for detecting small variations in the micromorphology [DeCandia et al. 1980].

(vii) Concentration dependence

At low concentrations the concentration dependence of diffusion coefficients can be expressed as follows [Park 1950]:

$$D = D_o e^{\alpha C} \qquad (3.11)$$

where D_o is the diffusion coefficient at zero concentration, C is concentration and α is a constant which gives a useful measure of the concentration dependence. This dependence varies with the nature of the polymer and penetrant. Good solvents are expected to loosen the polymer structure thus resulting in greater mobility. It is reported that as the polymer penetrant interaction parameter increases, the concentration dependence also increases [Kokes and Long 1953].

For a history dependent diffusion coefficient in the glassy state, the diffusion coefficient D_i resulting from the rapid change in concentration is given by:

$$D_i = D_o e^{aC} \qquad (3.12)$$

At constant concentration, it is assumed that the diffusion coefficient changes with time until a final value of equilibrium diffusivity, D_e, is reached:

$$D_e = D_o e^{bC} \qquad (3.13)$$

where b is a larger constant than a.

The time dependence results from an increase in free volume. It is assumed that the rate of increase of diffusivity obeys a first order law:

$$\left(\frac{\partial D}{\partial t}\right) = \alpha(D_e - D) \qquad (3.14)$$

where the rate constant α is also a function of concentration.

$$\alpha = \alpha_o e^{\sigma C} \qquad (3.15)$$

The overall differential equation relating D to C and t is then given

by:

$$\left(\frac{\partial D}{\partial t}\right) = \left(\frac{\partial D_i}{\partial C}\right)\left(\frac{\partial C}{\partial t}\right) + \alpha(D_e - D) \qquad (3.16)$$

By trial and error calculations, it is possible to obtain a, b, α, α_o and D_o giving a reasonable fit to sorption and desorption curves [Crank 1953].

A brief review of the free volume theory which predicts the dependence of diffusion coefficients on concentration will follow.

3.5. Theories Predicting the Dependence of Diffusivity on Concentration

3.5.1. General

It should be recognized by now that the diffusion coefficient is dependent on concentration. Assuming that diffusivity is either independent of concentration or changes linearly (as an approximation) with concentration is both unrealistic and inconsistent with experimental evidence. However, the prediction of the dependence of diffusivity on concentration has been a persistent problem. Such a problem is caused by our almost complete ignorance of the nature of the intermolecular forces which determine the interaction among different molecules and hence affect diffusivities. In addition, especially in the case of liquid diffusion, our very little knowledge

about the structure of liquids makes it impossible, at this stage, to formulate theories which can rigorously predict the dependence of diffusion coefficients on concentration. In fact, until now the true mechanism of the diffusion processes remains an unrevealed mystery. In addition, as indicated by Tyrrell [1969], there is a "deceptive simplicity" about the phenomenological description of the process as well as confusion about definitions which are not wholly absent even from the modern literature.

A number of theories such as Bueche's theory [1953], the theory of Cohen and Turnbull [1959], Barrer's Zone Theory [1957], Brandi's Theory [1959], and the Fujita's Free Volume Theory [1961] have been put forward to describe the dependence of diffusion coefficients on concentration in polymers. The Free Volume Theory due to Fujita [1961] appears to be the most successful and the most widely used theory for describing diffusional behaviour of organic penetrants in amorphous polymers.

3.6. Diffusion in Poly(ethylene)

Changes in polymerization conditions result in variations in the chemical structure of a polymer such as linear and branched polyethylenes. Consequently, its morphological and transport properties will largely depend on the conditions of polymerization. A low density polyethylene (LDPE) is expected to have a different set of

transport properties than its counterpart high density polyethylene (HDPE). Post polymerization treatment, such as drawing and annealing bring further morphological changes in polymers, which in turn alters their diffusion properties.

Extensive commercial use of this polymer has led to diffusion studies in polyethylene. Considerable contributions have been made in this field.

Michaels and Parker [1959] suggested that diffusion in semicrystalline polyethylene is given by the expression:

$$D = D_a/\tau\,\beta \qquad (3.17)$$

where D_a is the diffusion coefficient in completely amorphous polymer, τ is a geometric impedence factor, and β is a chain immobilization factor depending on the polymer morphology.

The factor, τ, is assumed to be independent of the molecular size and accounts for the need of a diffusing molecule to by-pass the crystalline regions, β is a size dependent factor which reflects the reduction in amorphous chain segment mobility caused by the proximity of crystallites.

Surprisingly, Baddour et al. [1964] noted a decrease in the factor τ for thermally annealed polymers, although there was an

increase in crystallinity in annealing. This was attributed to the deformation of the crystalline regions resulting from more extensive crystallites which created voids which are large enough to allow the passage of the diffusing molecules. Non-Fickian sigmoid sorption curves were also observed in semicrystalline polyethylene [Blackadder and Keniry 1974]. This was attributed to the slow relaxation process which also led to the time dependence in the surface concentration and secondly to the external stresses exerted by the swollen part of the system on the unswollen part. Further evidence of this is provided by recent studied on HDPE [Bischoff and Eyrer 1984]. It is suggested that in oriented semicrystalline polymers the mobility of the amorphous polymer is reduced to such an extent that even above T_g non-Fickian diffusion observed can be observed.

Results on sorption in linear polyethylene with varying degrees of crystallinity (0.48 - 0.82) show that in this polymer, the fractional free volume and the penetrant-polymer interactions are not affected by the increase in crosslinks provided by the crystallites upon drawing. However, the fractional free volume was reduced for the various penetrants studied [Ng et al. 1985].

The effect of drawing, crosslinking and annealing of LDPE on its transport properties was investigated by a number of researchers, e.g., Araimo et al. [1978] and DeCandia et al. [1980] and [1982]. The crosslinks introduced in the solid polymer did not influence the transport properties of the drawn material. The denser packing of the

amorphous component on drawing, as expected, reduces the fractional free volume and as a consequence has smaller sorption and diffusivity and a higher concentration dependence of diffusivity. This correlation between polymer morphology and transport properties, led to the suggestion that the transport properties can be used as a sensitive probe for detecting small variations in micromorphology of the polymer.

Studies on the use of polyethylene as a separation membrane were reported by Michaels et al. [1962]. They employed conditioned poly(ethylene) films for the separation of mixed xylenes, whereas recently Fleicher [1985] evaluated diffusion parameters for mixed solvents.

Despite this extensive work, it appears that no data for the effect of the diffusant size and shape on diffusion in LDPE are available. Therefore, in this work we set out to obtain information on such effects.

TABLE 3.1

Diffusion Coefficients of Some Gases in Various Rubbers at 25°C

Gas	$D \times 10^{10}\ m^2 s^{-1}$				
	Natural Rubber	Gutta Percha	Polybutadiene	Polychloroprene	Butyl Rubber
Hydrogen	10.20	5.0	9.60	4.31	1.52
Oxygen	1.58	0.70	1.50	0.43	0.08
Nitrogen	1.10	0.50	1.10	0.29	0.04
Carbon Dioxide	1.10	0.47	1.05	0.27	0.05

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3.7. Diffusion in Rubbers

The diffusion studies on rubbers date back to 1946 when Amerongen [1946], [1950] and [1964] measured the diffusion of a number of gases in various rubbers using the time lag and the sorption methods. Some of his results together with some other workers [Michaels and Bixler 1961 and Barrer 1957] are listed in Table 3.1. It shows that natural rubber has higher diffusivities than its cis form gutta percha. Also, the diffusion coefficients are higher in polybutadiene, than in chlorinated polybutadiene, whereas butyl rubber is least permeable to gases.

In the study of rubber/gas systems the activation energy of diffusion seemed to increase with increasing the diameter of the gas molecule, however, the relationship was not consistent. Vapour sorption studies on polyisobutylene [Prager and Long 1951] showed a linear relationship between log D and the concentration of the diffusant. The diffusion coefficient also increased with the size of the penetrant. This and other findings [Prager et al. 1953 and Aitken and Barrer 1955] showed no change in activation energy for the paraffin hydrocarbon/rubber systems. Mozisec [1971] evaluated the concentration dependence of diffusion coefficients for various solvents in natural rubber and polybutadiene using the microinterferometric method. The intrinsic diffusion coefficient of the solvents increased continuously with concentration, whereas mutual diffusion coefficients showed a maxima with concentration.

These findings pertain to unfilled and uncrosslinked rubbers, where the high values of diffusion coefficients are associated with the higher segmental mobility of the rubber molecules. When crosslinking and fillers are incorporated into the rubbers, then not only the segmental mobility is reduced or even disappeared, but additional factors also controlled the transport properties of rubbers.

3.7.1. Effect of crosslinks

It was found that as the degree of crosslinking increases, the diffusion coefficient decreases and the magnitude of the change is greater, the larger the penetrant molecule [Barrer and Skirrow 1948; Aitken and Barrer 1955]. The diffusion coefficient of nitrogen in natural rubber decreases from 1.08×10^{-10} to 1.1×10^{-11} m^2/s with 17% and 11.3% sulphur vulcanization, respectively. It is clear that the changes are due to the reduction of the segmental mobility, which is accompanied by a rise in the glass transition temperature. Hayes and Park [1955] studied the vapour sorption of natural rubber/benzene systems over a wide temperature range (0-90°C). The rubber samples were crosslinked to various degrees. It was found that the diffusion coefficient at zero penetrant concentration decreases monotonically on increasing the degree of crosslinking. However, when the diffusion coefficient at a higher volume fraction of penetrant, i.e. > 0.01, is plotted against the degree of crosslinking a maximum was obtained.

This maximum value of diffusion coefficient corresponds to the degree of crosslinking where natural rubber exhibited maximum tensile strength. The fact that the crosslinks introduced by sulphur vulcanization and through carbon-carbon bonds alter the cohesive energy of the polymer to a different extent, must be taken into account when studying diffusion in rubbers, for the sulphur crosslink seem to have less effect.

3.7.2. Effect of fillers

Fillers such as carbon black are important ingredients of many rubbers. They influence the mechanical as well as the transport properties of rubbers. The diffusion media is more polymeric but becomes heterogeneous and if the filler is not wholly "wetted" by the polymer, adsorption of diffusant can occur on the filler. Amerongen [1955] and [1964] obtained diffusion coefficients of various gases in natural rubber containing significant volume fractions of a range of fillers. There was a ten fold decrease in the diffusion coefficient of hydrogen, with 0.22 volume fraction of carbon black in natural rubber. On using various types of carbon black the diffusion coefficient varied between 1.9×10^{-10} to 7.2×10^{-10} m^2/s. This means that the filler particles are not always fully wetted by the polymer and thus the filled polymer may contain two dispersed phases. This type of situation has been also treated by Barrer and Chio [1965]. One would expect more complications in case of vapour and liquid diffusion in filled rubbers, since diffusivities are

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concentration dependent and solubilities are greater than in gases.

In addition to fillers, stabilizers are also added to the rubbers so during liquid sorption/desorption their extraction by the liquid may pose further problems.

3.8. The Free Volume Theory

The Free Volume Theory was developed by Fujita [1961]. According to this theory, the diffusion of a penetrant molecule in an amorphous polymer is only possible when the local free volume in the region of the penetrant molecule exceeds a certain critical value. The magnitude of such a local critical free volume depends on the size of the diffusant and is determined by the total free volume present in the system. In this theory, the thermodynamic diffusion coefficient, D^*, is related to the fractional free volume of the system, f_v, by the expression:

$$D^* = A\,RT \exp\left[- \frac{B}{f_v} \right] \qquad (3.18)$$

where A and B are constants which depend on the molecular size of the diffusant and on the polymer. The constant B increases with increasing the molecular size of the penetrant, hence, it leads to a decrease in the diffusion coefficient.

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The dependence on concentration, temperature, and on the glass transition temperature, T_g, results from the dependence of the fractional free volume, f_v, on these quantities. If the free volumes are assumed to be additive, then:

$$f_v = f_o + \beta'' \phi \qquad (3.19)$$

where f_o is the fractional free volume of the pure polymer, β'' is a parameter representing the contribution of the penetrant to the free volume and ϕ is the volume fraction of the penetrant.

At zero penetrant concentration, Equation (3.18) can be rewritten as follows:

$$D_o = A\,RT \exp\left[- \frac{B}{f_o} \right] \qquad (3.20)$$

The dependence of the fractional free volume on the glass transition temperature, T_g, and the temperature, T, can be deduced from the Williams et al. [1955] relationship:

$$f_o = f_g + \Delta\alpha (T - T_g) \qquad (3.21)$$

where f_g and $\Delta\alpha$ have the following universal values for amorphous polymers:

$$f_g = 0.025$$

$$\Delta\alpha = 4.48 \times 10^{-4}$$

The Free Volume Theory has achieved some success, however, it does not correctly predict the dependence of the mutual diffusion coefficient, D^V, of small penetrant molecules in amorphous polymers on temperature and concentration.

Recently, Vrentas and Duda and co-workers addressed the problems associated with the application of the Free Volume Theory to small penetrant molecules in a series of publications [1977, 1979, 1985a and 1985b]. They proposed the following expression:

$$D^V = D_{01}(1-\phi_1)^2(1-2\chi\phi_1) \exp\left[-\gamma \frac{(\omega_1 V_1^* + \omega_2 \zeta V_2^*)}{V_{FH}}\right] \qquad (3.22)$$

where γ is an "overlap" factor ranging from 0.5 to 1, ω_1 is the mass fraction of component 1, V_1^* is the specific local critical free volume required for the unit diffusion step of component 1, V_{FH} is the average hole free volume per gram of mixture, ϕ_1 is the volume fraction of the solvent, χ is the Flory-Huggins interaction parameter. D_{01} is a pre-exponential factor which depends on the temperature according to the following Arrhenius type expression:

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$$D_{01} = D_o e^{-(E_d/RT)} \qquad (3.23)$$

The quantity ς given in Equation (3.22) is defined by the following equation:

$$\varsigma = \frac{V_1^* M_1}{V_2^* M_j} \qquad (3.24)$$

where M_1 is the molecular weight of the solvent and M_j is the molecular weight of the "jumping" unit of the polymer.

Ju et al. [1981] tested Equation (3.22) using experimental data on poly(vinyl acetate), poly(methyl methacrylate), and polystyrene with chloroform, toluene, tetrahydrofurane, methanol and carbon disulphide. They concluded that Equation (3.22) provided an accurate description of diffusion in concentrated polymer solutions.

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4. EXPERIMENTAL

4.1. Mathematical Description of the Physical System

The physical system employed in this investigation consists of a very thin rectangular polymer film which is suspended inside an electrorecording microbalance. The film is saturated with the penetrant under investigation. As soon as vacuum is turned on, it is assumed that the surface concentration of the penetrant drops instantaneously to zero. The polymer film under consideration extends from $-\ell$ to $+\ell$ in the x-direction.

Since unsteady-state diffusion is being considered here, Fick's second law should be employed:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D \frac{\partial C}{\partial x}\right] \qquad (4.1)$$

with the following conditions:

(i) due to symmetry $\frac{\partial C}{\partial x} = 0$ at $x = 0$ and at all t

(ii) $C = 0$ at $x = \pm \ell$ and $t > 0$

(iii) $C = C_o$ at $t = 0$ and all x

The solution to Equation (4.1), using the separation of

variables technique leads to the following expression:

$$C = [A \cos(\lambda x) + B \sin(\lambda x)] \exp - [\lambda^2 Dt] \qquad (4.2)$$

Application of the boundary and initial conditions mentioned earlier, combined with the orthogonality property of the cosin functions leads to the following relations for λ and C:

$$\lambda = (2n+1)\frac{\pi}{2\ell} \qquad (4.3)$$

$$C = \sum_{n=0}^{\infty} \{\frac{4C_o(-1)^n}{(2n+1)\pi} \cos[(2n+1)\frac{\pi x}{2\ell}]\}\exp-[(2n+1)\frac{\pi}{2\ell}]^2 Dt \qquad (4.4)$$

The quantity of liquid remaining in the polymer film per unit area, Q_t, is given by:

$$Q_t = 2\int_t^{\infty} D\frac{\partial C}{\partial x}\Big|_{x=\ell} dt = \sum_{n=0}^{\infty} \{\frac{4C_o}{\ell[(2n+1)\frac{\pi}{2\ell}]^2}\}\exp-[(2n+1)\frac{\pi}{2\ell}]^2 Dt \qquad (4.5)$$

Since this series converges very rapidly, one can proceed using only one term. This represents the system in the later stages of desorption where $D = D_o$.

$$Q_t \simeq \left(\frac{16C_o\ell}{\pi^2}\right)\exp - \left[\left(\frac{\pi}{2\ell}\right)^2 D_o\, t\right] \qquad (4.6)$$

Initially, the amount of liquid contained in the polymer film is denoted by Q_o; where:

$$Q_o \simeq \frac{16C_o\,\ell}{\pi^2} \qquad (4.7)$$

If M_o, M_t, and M denote the weights of the dry film and the liquid contained in the film per unit area at times, 0, t, and ∞, respectively, then:

$$Q_t = M_t - M_\infty \qquad (4.8)$$

$$Q_o = M_o - M_\infty \qquad (4.9)$$

From the ratio of Equations (4.7) and (4.8) one obtains a linear plot of $\ln(M_t - M_\infty)$ versus t whose slope allows one to determine D_o.

4.2. Design of the Experimental Apparatus

The experimental apparatus employed in this study consists of a CAHN 2000 electrorecording balance, a vacuum system, an HP 3421A data acquisition system, a Sargent-Welch temperature controller (Model ST) and a Unitron 2200 (Apple II plus compatible) microcomputer with a

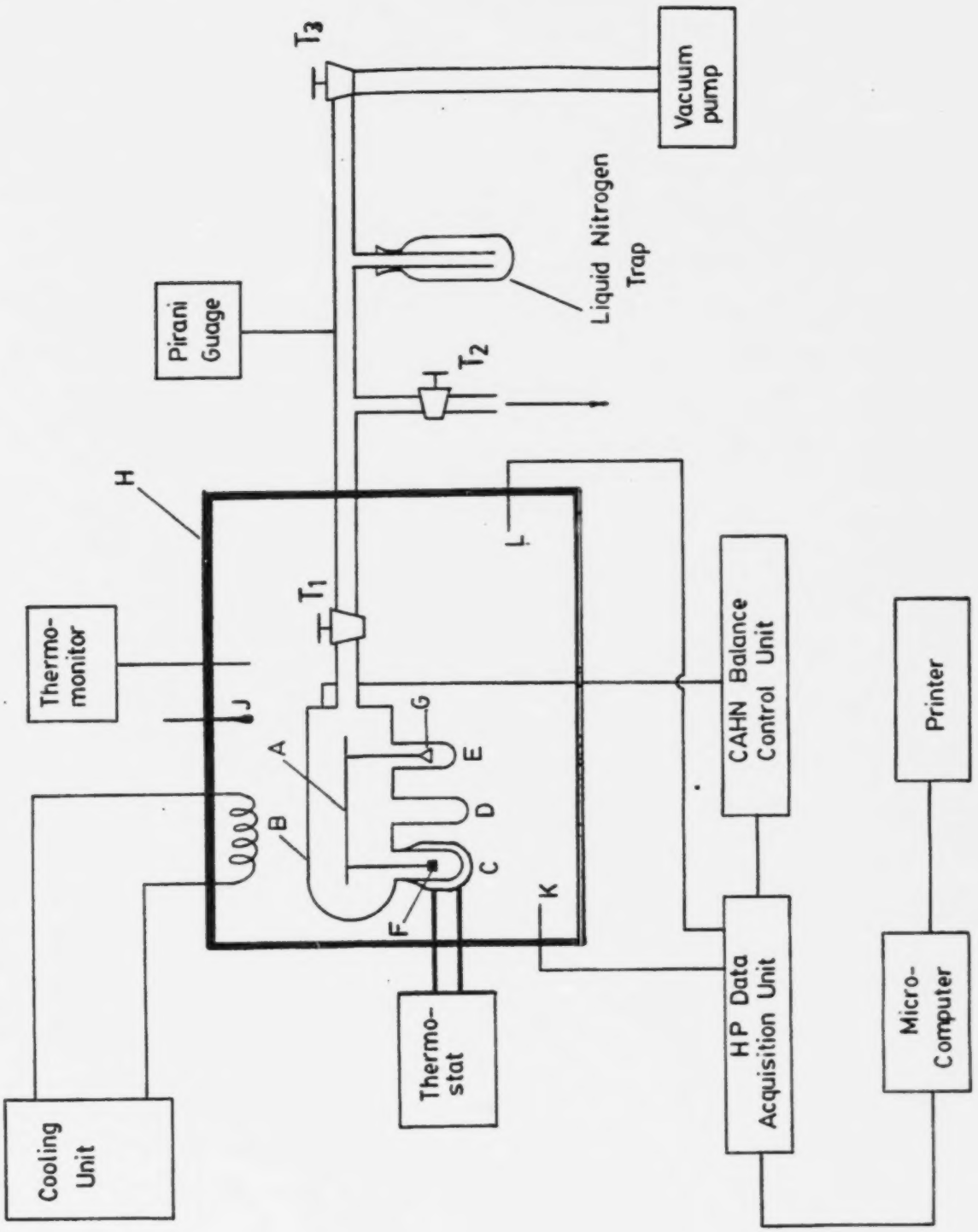

Figure 4.1- Schematic Diagram of the Experimental Set-up

printer.

A schematic layout of this apparatus is shown in Figure 4.1. The CAHN 2000 electrorecording microbalance consists of a control unit and a weighing unit, A. This weighing unit is enclosed by a glass vacuum bottle, B, having a vacuum outlet and three hangdown glass tubes, C, D and E. The polymer film F and counterweight stirrup G are suspended on the balance beam by means of hangdown wires and metal loops attached to the beam. The glass tube C, enclosing the polymer sample had a glass jacket, through which water flows at constant temperature, with a fluctuation of about $\pm$ 0.01 °C, is circulated from a thermostat. In order to avoid condensation, the whole weighing unit was fitted inside a metallic box, H. The temperature of this box is controlled by a Sargent-Welch Thermomonitor and an RMT cooling unit. The weighing unit is connected to the glass vacuum line through a cap. The vacuum line consists of a vacuum pump, liquid nitrogen trap, Pirani gauge and three taps T_1, T_2 and T_3. The weighing unit is evacuated by opening tap T_1, whereas tap T_2 is a vent and tap T_3 connects the system to the vacuum pump.

A precision mercury thermometer J and two thermocouples enable one to read the temperature at various points of the chamber. Normally, a variation of $\pm$ 0.3 °C is observed.

The data acquisition equipment consists of an HP 3421A data acquisition unit, a microcomputer and a printer. A 10 mv analog

output from the electrobalance is fed to the data acquisition unit where it is digitized and sent to the microcomputer. The two thermocouples K and L are connected to the data acquisition unit.

The printer provides a hard copy of the weight averaged over a selected time interval and the temperatures read by the thermocouples K and L averaged over the same selected time interval.

4.3. Experimental Procedure

Rectangular specimens of the polymer film with a hole at the top are cut. The size and hence the weight of the sample depends on the system under consideration. Care was taken to have a sample weight which could enable us to operate below the 100 mg range limit of the microbalance. Each of these samples are then immersed in a test tube containing the penetrant under investigation. This tube is already kept in a water bath at constant temperature. The sorption experiment is continued until sorption equilibrium is attained. The time required for this equilibrium depends on the polymer penetrant system; in most of the cases it did not exceed 24 hours. The equilibrium uptake of the penetrant is checked by periodically weighing the polymer film on a Mettler balance.

To start the desorption experiment the desorption chamber water circulating thermostat is set at the required temperature, and

the electrobalance is calibrated according to the procedure described by the manufacturer.

Once sorption is complete, the polymer film is removed from the liquid, and is sandwiched between two filter papers. This ensures the removal of the excess liquid from the surface of the polymer film, and thus a reproducible initial surface concentration of the penetrant can be achieved. The film is then suspended on the balance. The time between the removal of the film from the liquid up to suspending of the film on the balance should not exceed 10 to 15 seconds. The balance is immediately opened to the vacuum system at a pressure of 0.01 mm Hg and desorption kinetics are followed by monitoring the weight loss with time on the microcomputer.

Reproducibility of results is checked by conducting duplicate runs.

4.4. Materials

(i) Polymers

a. Low Density Polyethylene (LSPE): A CIL produced low density poly(ethylene) sheet (Grade 503) was used in this work. It had a thickness of 0.15 mm and a denisty of 918.0 kg/m.

b. Natural Rubber (NR): Three vulcanized natural rubber

films were provided by DREO. They had average thicknesses of 0.12, 0.25 and 0.32 mm. No information was provided on the composition of these films.

c. Bromobutyl Rubber (BIIR): DREO also provided us with three BIIR films. These films had average thickness of 0.11, 0.25 and 0.34 mm.

(ii) Penetrants

Gold label grade, dichloromethane, benzene, toluene, cyclohexane, o-xylene, m-xylene, p-xylene, chloroform, carbon tetrachloride, n-hexane, n-heptane, n-octane, n-decane, 2,2,4-trimethyl pentane (TMP) and trichloro-ethylene were obtained from Aldrich Chemical Company, and were used without further purification.

Unleaded gasoline, diesel fuel and kerosene oil were purchased from the market, and were used as such. Aviation fuel was provided by DREO.

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5.1. General

The experimental results obtained in this investigation and their interpretation are presented in this part of the report. The following section is concerned with a brief review of the procedures employed at DREO for obtaining penetration times. This is followed by an analysis for the penetration data which were provided by DREO.

The details of a study on the diffusion of organic molecules and battlefield contaminants in rubbers and plastics is contained in the final section of this part of the report.

5.3. Diffusion of Organic Molecules and Battlefield Contaminants in Rubbers and Plastics

The results of this part of the investigation are reported in three subsections. The first subsection deals with the diffusion of penetrants of various size, shape and chemical nature in LDPE. In the second subsection, the diffusion of saturated paraffin hydrocarbons in LDPE is reported, whereas the last subsection is concerned with the various kinds of fuels diffusing in crosslinked natural rubber and bromobutyl rubber.

All the results reported here, were obtained by following the desorption kinetics. In the final stages of desorption experiments, the concentration of the penetrant tends to be zero, therefore a plot of $\ln(M_t - M_\infty)$ versus time approaches a straight

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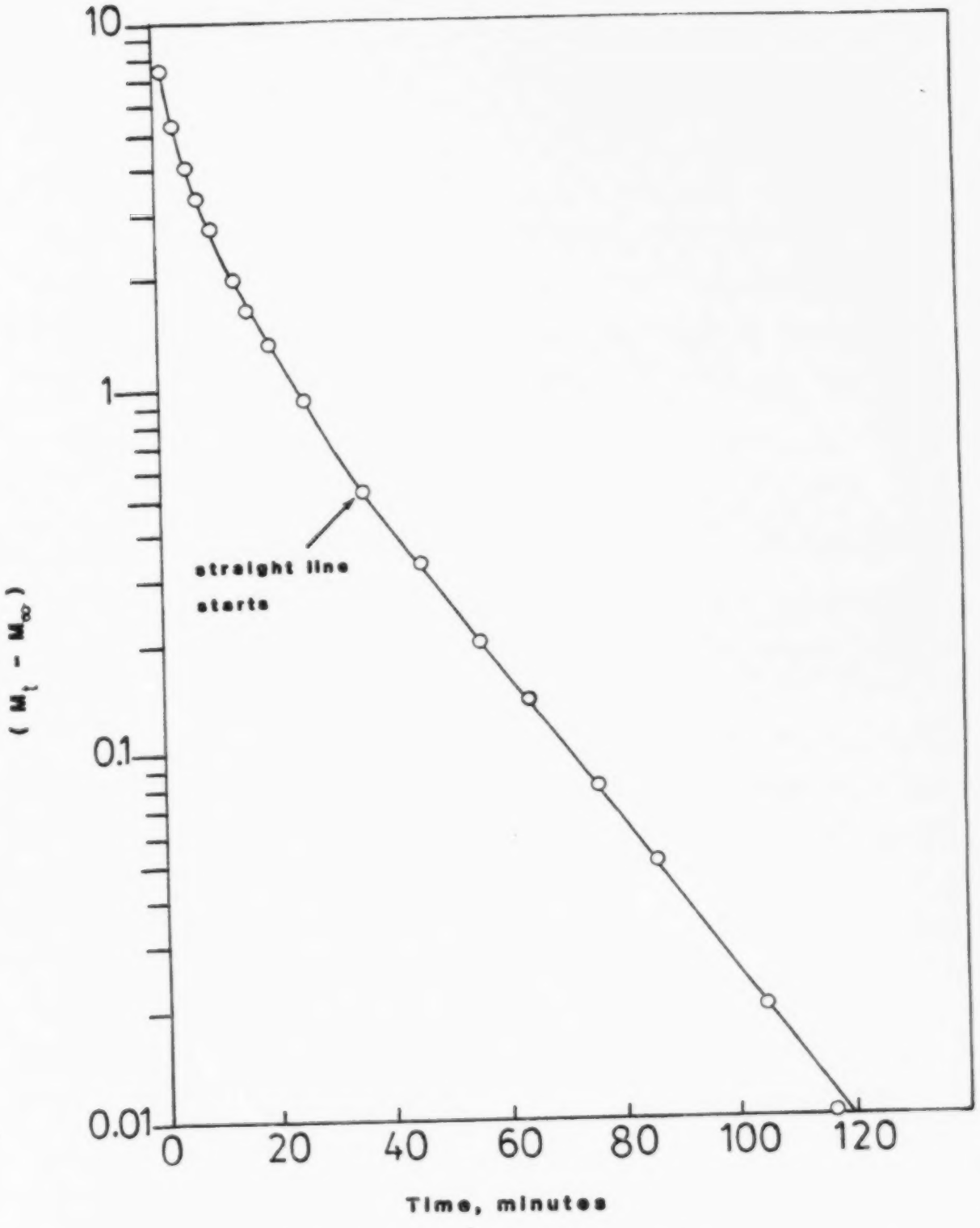

Figure 5.6- Typical Plot for the Desorption of Chloroform at 25° C

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TABLE 5.4

The Diffusion Coefficients, D_o, of Various Penetrants in LDPE at 25°C

Penetrant	Molar Volume of the Penetrant $\times 10^{-6}$ m^3 mol^{-1}	$D_o \times 10^{12}$ m^2 s^{-1}
Dichloromethane	63.6	5.062
Chloroform	80.2	1.783
Benzene	88.9	1.977
Carbon tetrachloride	96.5	0.656
Toluene	106.3	1.813
Cyclohexane	108.0	0.607
o-Xylene	118.0	0.940
m-Xylene	122.3	1.459
p-Xylene	122.6	1.567
n-hexane	130.7	1.256

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line, whose slope is given by the following expression:

$$\frac{d}{dt}[\ln(M_t - M_\infty)] = -\frac{D_o \pi^2}{4\ell} \qquad (5.2)$$

where M_t is the amount of the penetrant in the polymer film at time t and M_∞ is the equilibrium amount attained theoretically after infinite time per unit area; 2ℓ is the thickness of the polymer film. In this work, D_o has been evaluated from the final part of the $\ln(M_t - M_\infty)$ vs time plots. A typical plot for chloroform at 25 °C is shown in Figure 5.6. In each case, the linear portion of these plots is fitted to the best straight line by using the least-squares method. The value of the slope is determined and used to calculate D_o from Equation (5.2).

Alternatively, D_o can also be obtained from sorption data, where plots of concentration dependent diffusion coefficients are extrapolated to zero concentration, but the extrapolation procedures are always subject to errors of various magnitudes. The desorption method reported here, does not suffer from this disadvantage and duplicate experiments produced consistent results.

5.3.1. Diffusion of various penetrants in LDPE

The D_o values of penetrants in LDPE at 25 °C, along with their molar volumes are reported in Table 5.4. It can be seen that, apart from three exceptions (carbon tetrachloride, o-xylene and cyclohexane) diffusion coefficients decrease with increasing the size

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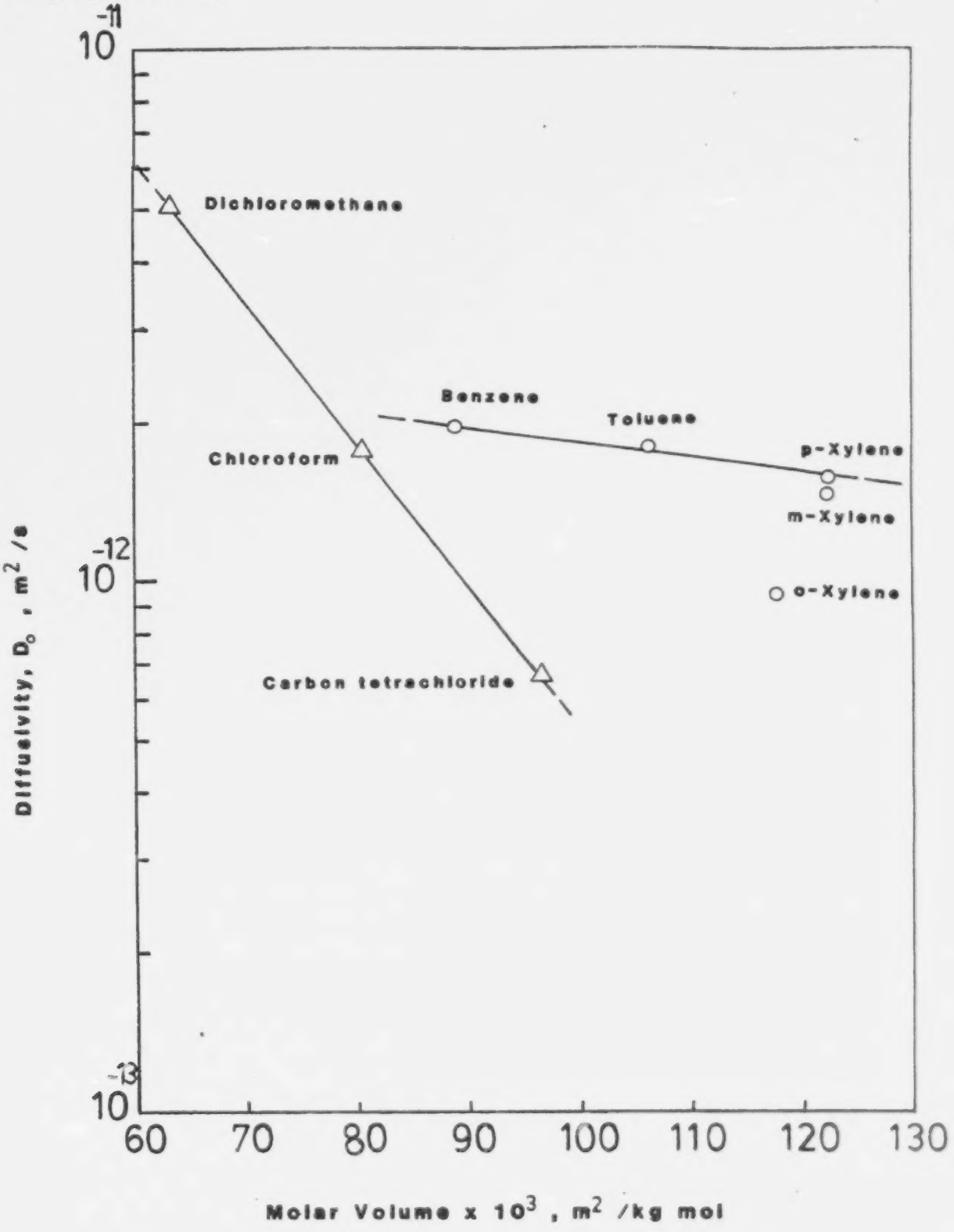

Figure 5.7- Variation of D_o with Molar Volume

of the penetrant molecules and tends to level off in the region of m-xylene and n-hexane. This is consistent with previous findings, e.g., Saleem [1977], where it was suggested that as the diffusant size increases, the dependence of D_o on the molar volume of the penetrant molecules becomes less pronounced. This appears to be generally true, however, another way for correlating the size with D_o involves comparing the penetrants of increasing size with similar basic chemical structure, thus annuling the effect of the latter to a greater extent. The change in log D_o with the molar volume of the two families of the penetrants is shown in Figure 5.7. Although the study pertains to a narrow size range of the penetrant, still the decrease in log D_o in each case is very evident. A further increase in the size of this series of penetrants may induce shape, length aand diameter effects.

Figure 5.7 also reveals the shape effect of positional isomers of xylene. This is more obvious in the case of o-xylene. In spite of its smaller size compared to its counterparts, it has the lowest diffusion ccefficient. It appears that the two adjacent methyl groups distort its symmetry and thus make it less mobile. This effect is less marked in m-xylene and tends to disappear in p-xylene where molecular symmetry is restored. Earlier on, Michaels et al. [1962] suggested a method for the separation of a mixture of xylenes through a conditioned poly(ethylene) film, nevertheless, they did not report any diffusivity data for their system.

Chlorinated penetrants also show a decrease in D_o with increasing penetrant size as can be seen in Figure 5.7. The magnitude of this decrease is, however, about three times that of benzene and its methyl substitutes. This can be attributed to the bulky chlorine atom which markedly reduces the mobility of the penetrant molecule. The chemical diversity between the chlorinated penetrants and the polymer backbone can be another reason for such a strong dependence of log D_o. An increase in the number of carbon atoms in the penetrant molecule seems to reduce its probability of findings or creating an appropriate "gap size" between the adjacent polymer chains.

Cyclohexane has a lower diffusion coefficient than toluene, although their molar volumes are almost the same (cf. Table 5.4). This is due to the cyclic nature of cyclohexane which makes it a rigid molecule as had been reported in earlier works for other polymers [Brown etal. 1973 and Park and Saleem 1984]. On the other hand, n-hexane has the largest size among the series of penetrants studied, but its linear and flexible molecule compensates for its size and results in a lower value of D_o. It is close to the D_o of the smaller but more rigid m-xylene molecule.

Detailed findings of the effect of temperature on diffusion in LDPE is reported in the next section; however, the results on the diffusion of toluene and n-hexane in the limited temperature range (25 45 °C) are included here.

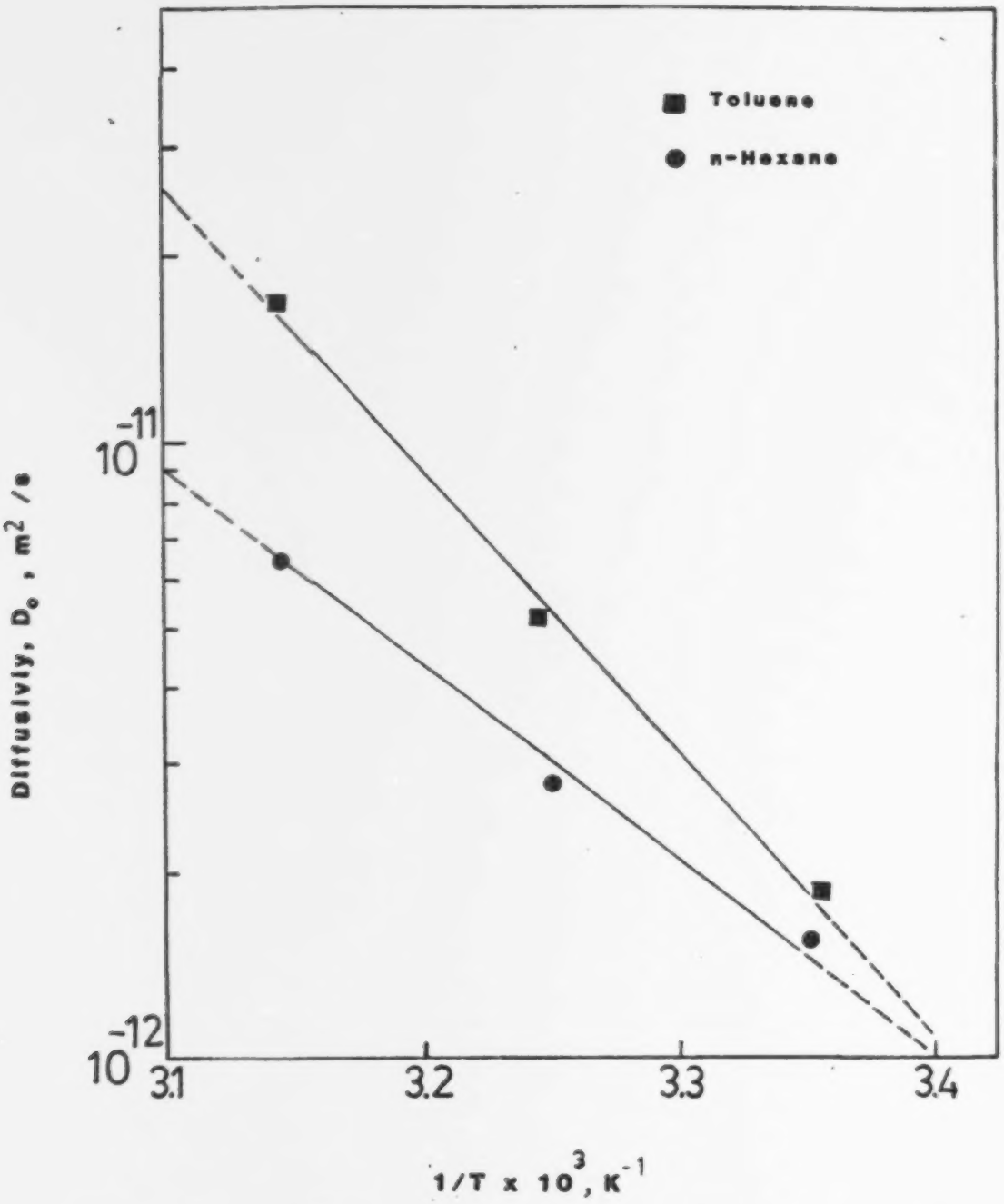

Figure 5.8- Dependence of D_o of n-Hexane and Toluene in LDPE on Temperature

The activation energy of diffusion is given by the Arrhenius type relationship (cf. Equation 3.10). The plots of log D_o versus 1/T for toluene and n-hexane are shown in Figure 5.8. Since this study pertains to a narrow temperature range, it can be assumed that the activation energies are indepdent of temperature. Estimates of activation energies from these plots yield the values of 87.0 and 65.4 kJ/mol for toluene and n-hexane, respectively. The low activation energy for the larger n-hexane molecule is rather surprising. Previously, it had been suggested [Kokes and Long 1953] that the activation energy of diffusion increases with the size of the penetrant until a value approximately equal to the activation energy of viscous flow is reached, after which it remains constant. Assuming that the value of viscous flow has not been reached in the system under study, the lower activation energy for n-hexane can, probably, be associated with the flexibility and smaller diameter of such a molecule. Also, the similarity in shape between n-hexane and the larger molecule of poly(ethylene) could lead to the high frequency of finding the "hole" of an appropriate size in the larger but analogous polymer chain thus leading to relatively lower activation energies.

5.3.2. Diffusion of paraffin hydrocarbons in LDPE

The diffusion studies in LDPE were extended to other penetrants of larger size, like n-heptane, n-octane, n-decane and TMP, over a temperature range of 25-50 °C. The D_o values obtained through the desorption technique, at various temperatures for the five penetrants are reported in Table 5.5.

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TABLE 5.5

Diffusion Coefficients, D_o, and Activation Energy, E_d,

for Diffusion of Saturated Hydrocarbons in LDPE

Penetrant	Molar Volume of Penetrant x 10^6 m^3/mol at 25°C	D_o x 10^{12} m^2/s					Activation Energy, E_d, kJ/mol	A x 10^{10} kJ/mol	B
		Temperature °C							
		25	35	40	45	50			
n-Hexane	130.7	1.256	3.055	4.659	6.503	10.887	67.7	8.8	0.525
n-Heptane	146.5	0.973	3.336	4.483	6.738	9.024	70.9	15.6	0.551
n-Octane	162.5	0.861	2.607	4.315	7.800	9.954	80.7	105.7	0.628
n-Decane	194.9	0.429	1.862	3.273	5.451	8.880	96.8	1782.6	0.755
TMP	165.1	0.320	0.728	1.432	2.387	4.267	96.2	1589.0	0.783

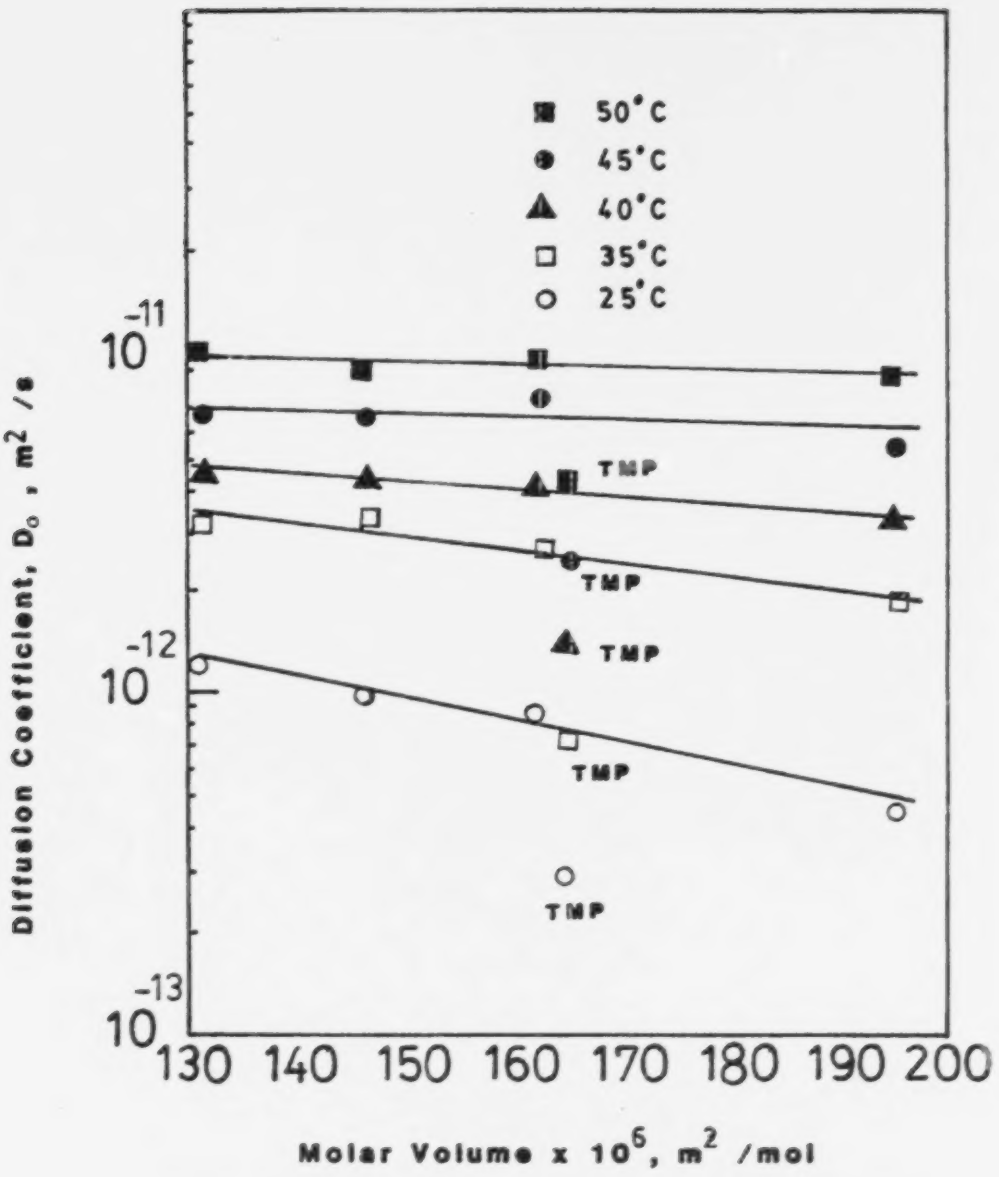

Figure 5.9- Variation of the Diffusion Coefficient, D_o , with the Molar Volume of Penetrants at Different Temperatures

5.3.3. Effect of the size of paraffin molecules on diffusion coefficients

Figure 5.9 shows the dependence of the diffusion coefficient on the size of a penetrant molecule. There is a decrease in D_o as the size of the diffusing molecule increases. As shown in Figure 5.9, the relationship between log D_o and the molar volume of this series of hydrocarbon penetrants is linear. The ratio between log D_o and molar volume, obeys the order: chlorinated solvent > hydrocarbons > benzenes. This indicates that if the hydrocarbons are investigated in a narrow size range like that of chlorinated solvents, one may not observe any size effect. However, the effect of increasing the length of these molecules is very evident. This suggests that in order to evaluate the penetrant size effect on diffusion in polymers, penetrants of similar chemical nature provide more meaningful information than molecules of increasing size but of diverse chemical structures.

It is very clear that the dependence of D_o on the size of the penetrant decreases with increasing the temperature and almost becomes insignificant at 50 °C. This was expected since an increase in temperature will accompany an increase in the free volume of the polymer. Earlier findings [Brown and Park 1970 and Saleem 1977] also suggest that the dependence of D_o on the size of the penetrant diminishes with increasing the temperature.

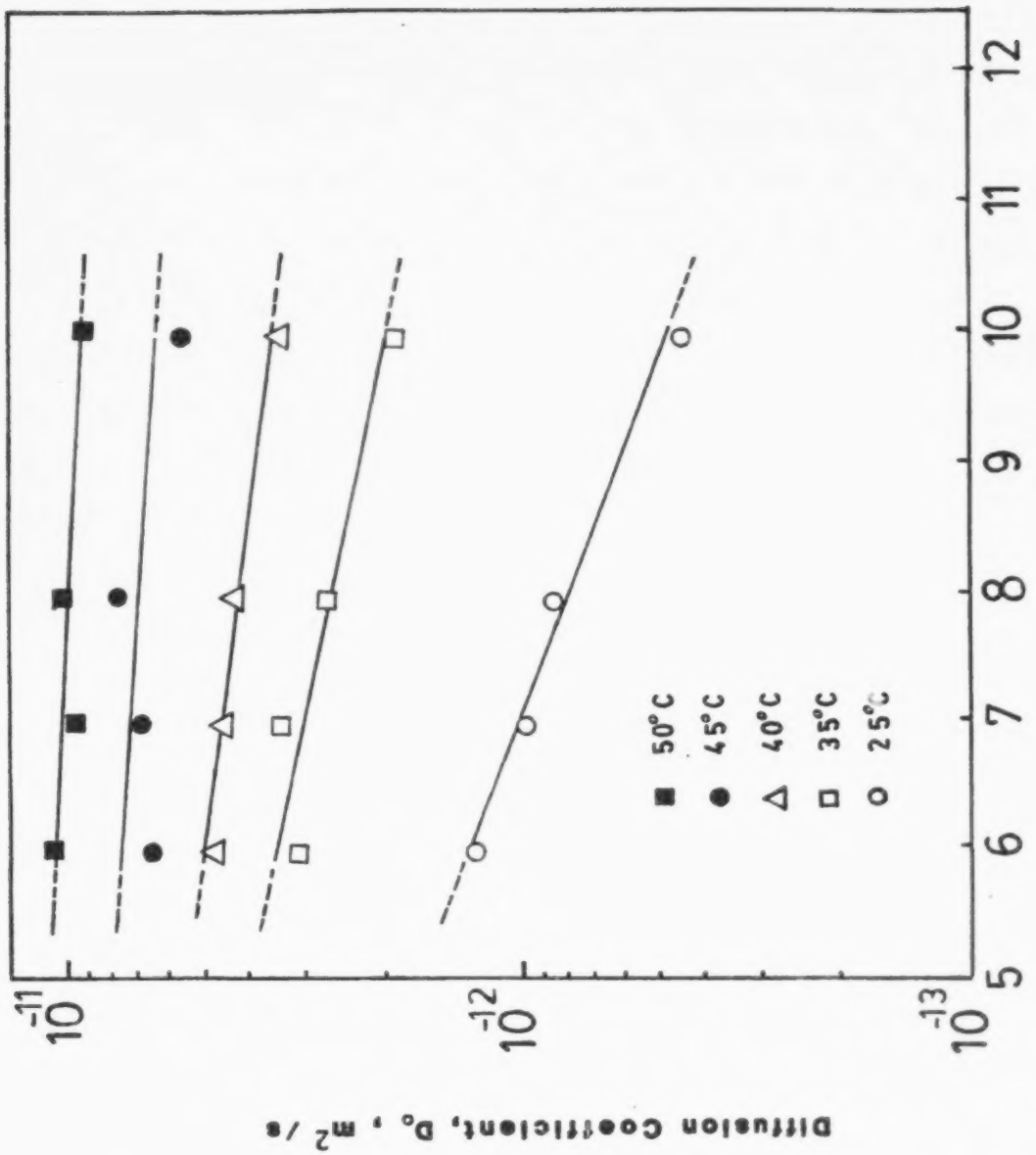

Figure 5.10- Variation of the Diffusion Coefficient, D_o , with the

Figure 5.10 shows a plot log D_o against the number of carbon atoms in CH-$(CH_2)_n$-CH. Again, a decrease in log D_o is evident. Fujita et al. [1960] findings for the alkyl acetate series in poly(methylacrylate) were replotted by Brown and Park [1970] and their plot of log D_o versus the number of carbon atoms in ester groups shows a ten fold decrease in D_o for four carbon atoms, whereas in our case there is about 1.5 fold decrease in this range. This difference is understandable considering the nature of these two different systems; however, the relationship is linear in both cases.

5.3.4. Effect of the shape of the penetrant molecules on diffusion coefficients

Through a number of studies [Brown and Park 1970; Brown et al. 1973, Saleem 1977 and Saleem et al. 1986], it has been established that a penetrant molecule has a profound effect on the diffusion in polymers. A linear and flexible molecule should be expected to diffuse more quickly than a rigid and unsymmetrical molecule. The rigidity effect of TMP has already been compared, using two different techniques, with the long n-hexadecane molecule diffusing in poly(butadienes). Therefore, in this work we observed the shape effect of isomeric paraffin hydrocarbons of comparable size. It was found that, at all the temperatures studied, the values of D_o for TMP are considerably lower than the expected values of a linear molecule of the same size.

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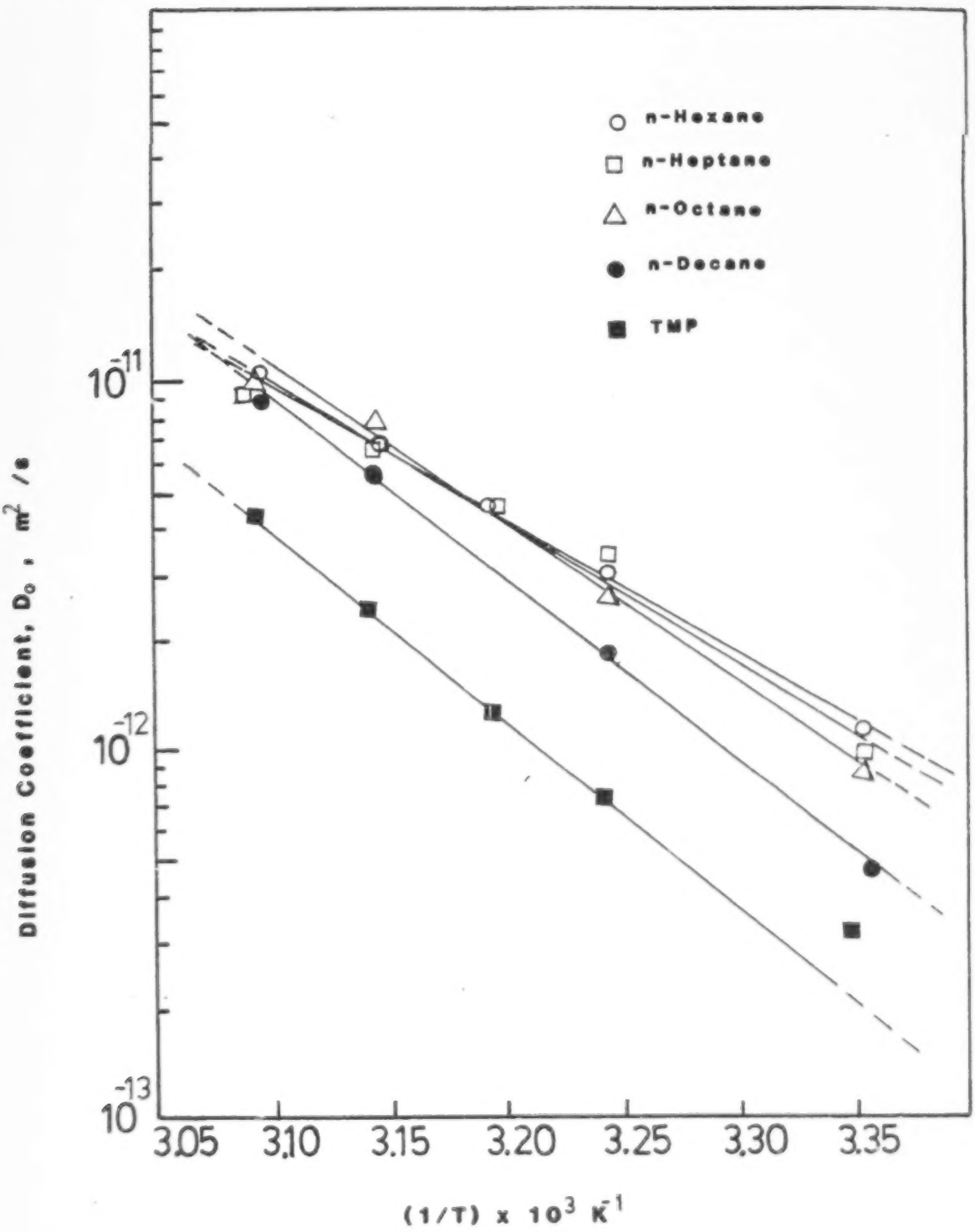

Figure 5.11- Temperature Dependence of the Diffusion Coefficient, D_o , of the Various Penetrant in LDPE

If we denote the diffusion coefficient of TMP, expected just on size consideration, by D_e and its actually observed diffusion coefficient by D_o then the ratio D_e/D_o at 35 °C is about 3.3. This ratio for TMP drops to 2.2 at 50 °C but the difference still persists. The effect of the length of the corresponding linear molecules tends to disappear at higher temperatures. This variation for TMP must be due to its large diameter. This would then suggest that the effect of the length of the molecule is less than the effect of diameter. The pendant methyl group in TMP with its larger diameter still cannot locate an appropriate "hole size". It appears that this effect for the TMP molecule will be observed until a temperature is reached at which enough free volume becomes available to allow its complete mobility.

Conversely, when penetrant molecules are of comparative diameter but of varying length, then the effect of the length of the molecule will play a dominant role. This was the case for the flexible and long molecule of n-hexadecane [Saleem 1977] whose measured diffusion coefficient in plasticized PVC is much lower than would have been expected on the basis of its diameter.

5.3.5. Effect of temperature on diffusion coefficients

The activation energies, E_d, of diffusion are obtained from the usual Arrhenius expression (Equation 3.10). Figure 5.11 indicates that the plots of log D_o against the corresponding 1/T are linear

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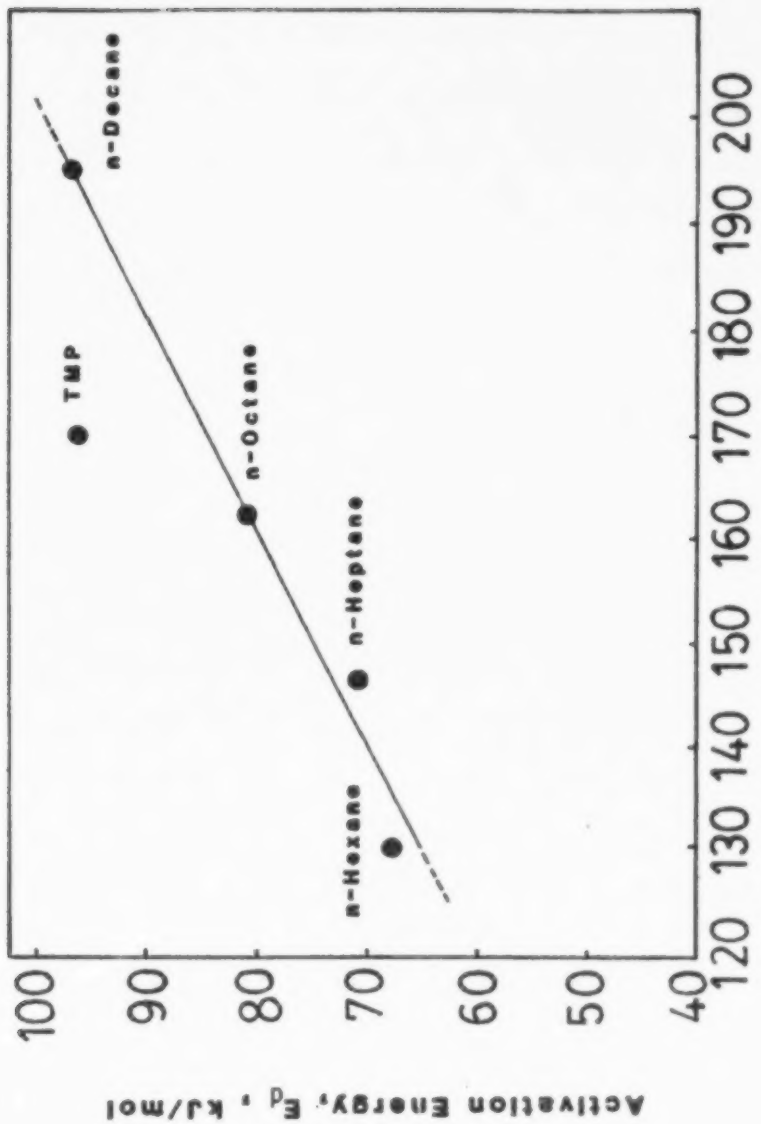

Figure 5.12- Variation of the Activation Energy of Diffusion, E_d , with the Molar Volume of Penetrants

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which confirms that E_d is independent of temperature in the covered temperature range. For n-hexadecane, n-heptane and n-octane these plots tend to overlap with each other around a temperature of 40 °C. This indicates that there is a possibility that if the experiments are conducted above 50 °C, one may not observe any distinction between the activation energies of these penetrants. The larger n-decane molecule and the relatively rigid TMP molecule do not demonstrate this effect in this region. In spite of repeated experiments the D_o of TMP at 25 °C lies above the Arrhenius plot and is probably associated with the error which is encountered during the longer desorption time required for this penetrant at 25 °C.

The activation energies of all the five penetrants are calculated from the best fitted straight lines. The results are given in Table 5.5. The variation in activation energy with increasing the molecular size of the penetrant are shown in Figure 5.12. There is a linear increase in E_d with increasing the size of the penetrant molecule. On previous occasions it was noticed that there was no increase in activation energy for diffusion of poly-isobutylenes and natural rubber [Aitken and Barrer 1955 and Prager and Long 1951]. This difference between our and previous findings, should be attributed to the nature of the polymer and the size of the penetrant under consideration.

Kokes and Long [1953] suggested that the activation energy of diffusion shows an increase with the size of the penetrant molecule

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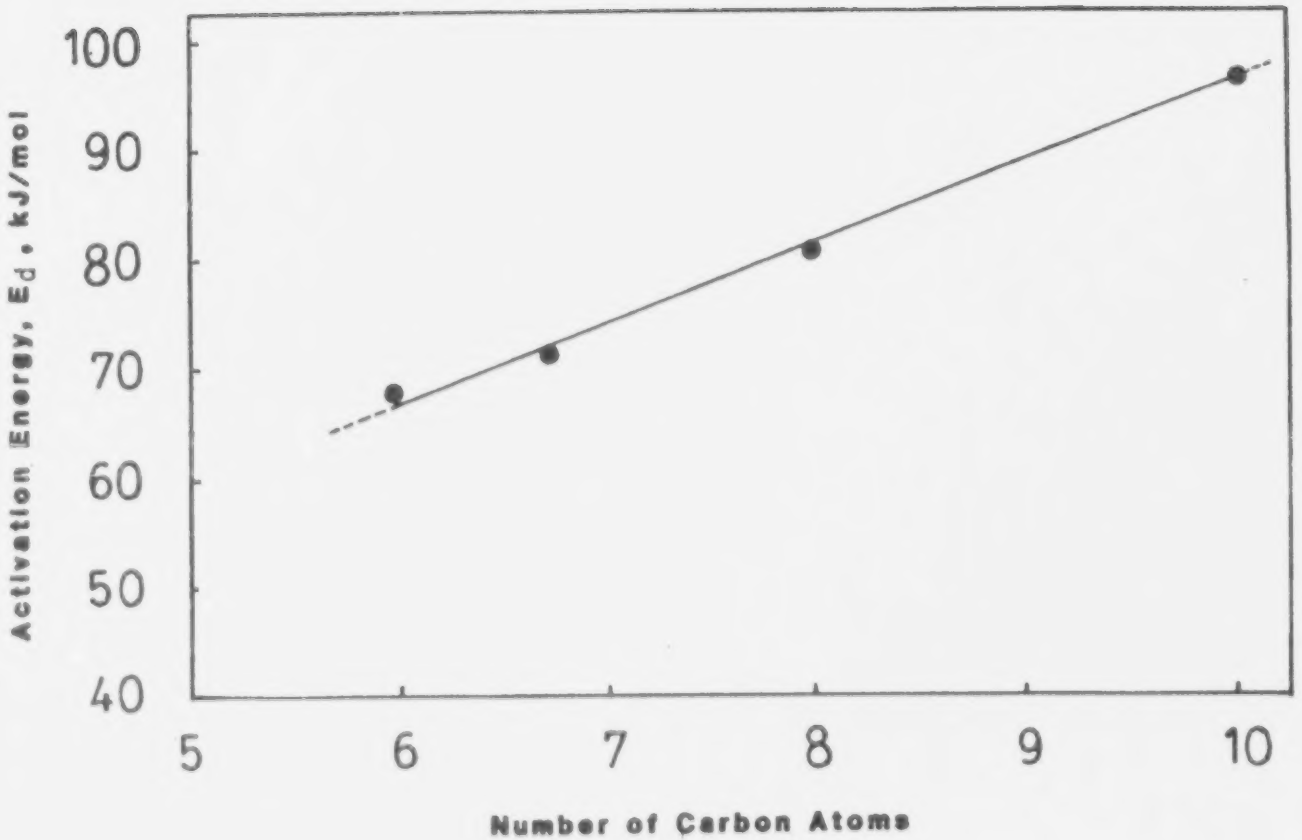

Figure 5.13- Variation of the Activation Energy of Diffusion, E_d , with the Number of Carbon Atoms in $CH_3 (CH_2)_n CH_3$ Hydrocarbon Molecule

until a value approximately equal to the activation energy of viscous flow, E_v, is reached. This is true for an amorphous polymer with a large fractional free volume; which is the case for soft polymers like rubber where no activation energy change is expected for small penetrants like n-butane, n-pentane and their isomers. Similarly, there was no difference between the activation energies for benzene and n-hexadecane in highly plasticized poly(vinyl chloride). The activation energy for the diffusion of n-hexadecane is greater than that of benzene in poly(vinyl chloride) with low plasticizer content. In LDPE the partial crystallinity will reduce the available free volume and consequently the relatively larger penetrant molecules, under study, will require more activation energy. Figure 5.13 also shows an increase in the activation energy with increasing the number of (CH_2) groups in the series. There is no evidence of activation energy reaching the value of viscous flow. For each additional CH_2 group there is an increase of about 7.5 kJ/mol in the activation energy.

The TMP molecule has three pendant methyl groups which contribute to its larger diameter and consequently it requires a larger "hole size". Therefore, it has a higher activation energy than its isomer n-octane of a similar size.

5.3.6. Application of the free volume theory

The dependence of the diffusion coefficient on

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concentration, temperature and on the size of the penetrant can be explained by the free volume theory. In this theory, however, free volume is not clearly defined. Consequently, it is difficult to provide quantitative predictions. Nevertheless, semi-quantitative estimates of the free volume parameters A and B in Equation (3.20) can be made, provided that the fractional free volume, f_o, is known.

The fractional free volume can be evaluated from the WLF expression given by Equation (3.21) where the universal values of $f_c = 0.025$ and $\Delta\alpha = 4.48 \times 10^{-4}$ can be used. Equation (3.21) is valid for only amorphous polymers, whereas LDPE is a partially crystalline polymer. An allowance can be made from this crystallinity and Equation (3.21) can be rewritten as [Saleem et al. 1986]:

$$f_o = [f_g + \alpha(T - T_g)](1 - \phi_c) \qquad (5.3)$$

where ϕ_c is the volume fraction crystallinity of LDPE.

Amorphous poly(ethylene) is reported to have a glass transition temperature of -75 °C [Manaresi and Giannella 1960]. No attempt was made to determine the crystallinity of LDPE, used in this study. It has the same density (918 kg/m) as reported by Kreituss and Frisch (1981), where its fractional crystallinity, ϕ_c, is reported to be 0.50. Therefore, this value can be safely used in our calculations of the fractional free volume, f_o. This obviously involves the following assumptions:

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TABLE 5.6

Free Volume Estimates for LDPE at Various Temperatures

Temperature °C	Fractional Free Volume, f_0
25	0.0365
35	0.0389
40	0.0401
45	0.0413
50	0.0425

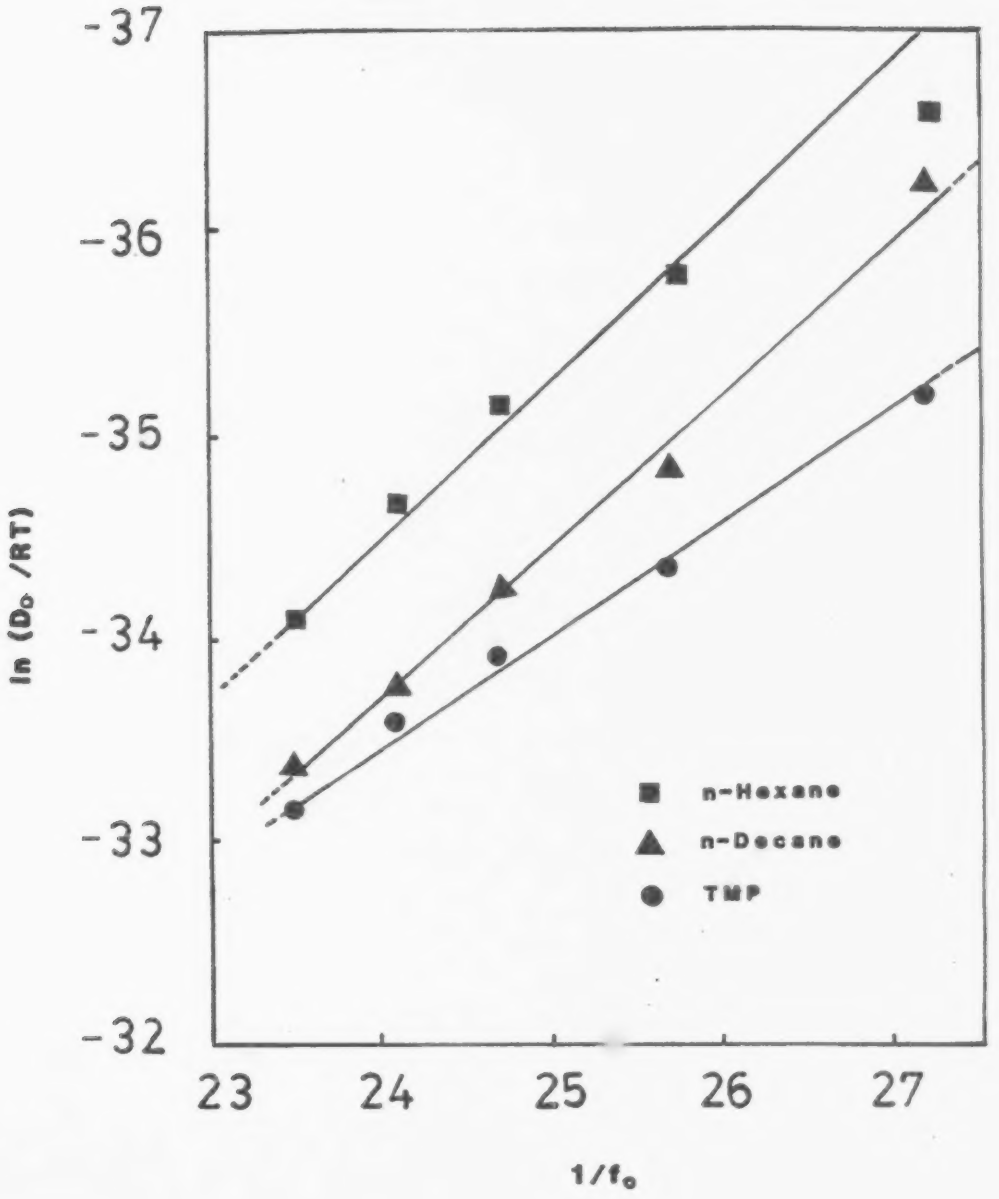

Figure 5.14- Variation of $\ln(D_o / RT)$ with $1/f_o$

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(i) WLF free volume is considered to be equal to free volume, f_o, given by Equation (3.20)

(ii) the crystalline fraction of the polymer is assumed to be impermeable and thus does not contribute to the free volume of the polymer, and

(iii) previous swelling of the polymer has no effect on the polymer morphology.

In any case, the contribution of the crystalline portion of the free volume, if any, will be very small and can easily be ignored. Also, the D_o values were obtained at very low concentrations; theoretically zero concentration. Thus, the net effect of the solvent will be negligible.

In this way, the free volume, f_o, values were obtained through Equation (5.3) and are reported in Table 5.6 for LDPE at all the temperatures studied.

When D_o and f_o are known, the values of the parameters A and B can be obtained through Equation (3.20). A plot of $1/f_o$ against $\ln(D_o/RT)$ gives a straight line with a slope equal to B and intercept equal to A. The f_o values, given in Table 5.6 were used to construct these plots. An example of this is given in Figure 5.14. The B and A

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values obtained for the various penetrants are given in Table 5.5. It can be seen that B increases with increasing the size of the penetrant molecule, which is consistent with the free volume theory. Generally, a decrease is expected in A but in this case, A also increases with increasing the size of the penetrant. This is rather surprising but similar results were reported for polymers below their glass transition temperatures [Saleem 1977] and perhaps the same applies to partially crystalline polymers. This also suggests that B largely depends on the penetrant size whereas A appears to be largely polymer dependent.

Our free volume estimate for LDPE is lower than the reported value of 0.066 by Fleisher [1985], but is almost in agreement with the value of 0.038 obtained at 25 °C through the sorption method by Fels and Li [1974]. If the crystalline fraction is not taken into account, our results match those reported by Fleicher [1985]. The value of B for heptane was found to be 0.221 [Fels and Li 1974], which is much lower than our estimated value of 0.551, but Fels and Li found this value by an extrapolation technique which according to the authors is subject to errors of considerable magnitudes.

Estimates of viscous energy of flow, E_v, can also be made from the knowledge of the activation energy and the parameter B. The zero shear melt viscosity of the polymer, η_o, is given by:

$$\eta_o = A \, Exp(1/f_o) \qquad (5.4)$$

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TABLE 5.7

Data on Diffusion of Various Penetrants in Natural Rubber at 25 °C

Thickness of the BR Film	Original Weight of the Film	Weight of the Film After Desorption	Weight Loss	Equilibrium Concentration of the Penetrant C	Best Mean Value of C	Diffusion Coefficient $D_o \times 10^{12}$	Best Mean Value of $D_o \times 10^{12}$
mm	mg	mg	%	g/g	g/g	m^2s^{-1}	m^2s^{-1}
				GASOLINE			
0.12	75.1	70.5	6.13	1.358		2.680	
0.25	57.1	53.4	6.32	1.652		5.735	
0.25	52.1	48.7	6.30	1.445	1.335	6.490	6.063
0.32	76.3	71.2	6.68	1.347		5.963	
0.32	74.0	69.4	6.20	1.301		8.079	
				TRICHLOROETHYLENE			
0.12	22.6	22.6	0.00	7.92		22.520	
0.12	13.5	13.5	0.00	5.71		19.750	
0.25	13.8	12.9	6.52	5.68	6.570	27.860	24.128
0.25	22.3	20.6	7.62	6.89		28.850	
0.32	22.6	20.1	11.06	6.65		21.930	
				AVIATION FUEL			
0.12	31.6	29.8	5.69	2.50		1.685	
0.25	33.5	31.8	5.07	2.64	2.590	3.948	5.273
0.25	22.9	22.2	3.05	2.58		6.249	
0.32	17.1	16.4	4.09	2.65		5.622	
				DIESEL FUEL			
0.12	39.0			2.72	2.72	0.016	0.016
				KEROSENE			
0.12	44.6	43.0	3.58	2.752	2.470	0.387	0.367
0.13	54.2	52.2	3.69	2.203		0.347	

$$C = \frac{\text{g of penetrant}}{\text{g of rubber}}$$

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Comparing this Equation with Equation (3.20), Fujita et al. [1960] obtained the following relationship for the energy of viscous flow:

$$E_d = E_v - \frac{RT}{B} \qquad (5.5)$$

Substituting the E_d and B values from Table 5.5 into Equation (5.5) yields a value of 125 kJ/mol for the energy of viscous flow of normal paraffin hydrocarbons, which corresponds to a linear hydrocarbon molecule with 14 carbon atoms. Until that limit of molecular size is reached there is a possibility of increase in activation energy with the increasing size of the penetrant molecule diffusing in LDPE.

5.3.7. Diffusion of fuels in rubbers

Diffusion coefficients of various fuels in rubbers were obtained in the same way as described for polyethylene in the previous subsections. In this case, however, loss in weight of the polymer films were noticed after desorption. This loss in weight was quantified in each case.

(i) Natural Rubber (NR)

Results of the diffusion of gasoline, trichloroethylene, aviation fuel, diesel fuel and kerosene in natural rubber films of various thicknesses are reported in Table 5.7. As expected, the equilibrium uptake of solvents is high, especially in the case of

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trichloroethylene. Since trichloroethylene has a relatively high density, so in terms of its volume fraction this extraordinary high figure can be justified. The overall high uptake by the rubber network with enough segmental mobility of the polymers with porous carbon black particles is not surprising. Similar high vapour uptake of benzene in rubber has been reported previously [Hayes and Park 1955].

Another interesting feature is the loss of weight of the polymer films. With a few minor exceptions, there is a loss in each case. The most probable reason for this can be the oxidation of some of the additives during the sorption process. In this case, the unwetted filler may ooze out into the liquid pool, or a soluble additive like a stabilizer goes into the solution. Alternatively, it can be argued that some of the additives are extracted from the film during the desorption process at low pressures. This is unlikely to happen, for this will result in lower values of diffusion coefficient, which is not the case. Nothing conclusive can be said about it until the full information on the composition of the natural rubber samples are available and some comparative studies are made.

The effect of the thickness of natural rubber films on diffusion coefficients does not seem to be very consistent. In case of gasoline there appears to be some evidence that the diffusion coefficients increase with thickness, but this will be contrary to the previous findings of Prager and Long [1951], where reduced conjugate

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TABLE 5.8

Data on Diffusion of Various Penetrants in Bromobutyl Rubber at 25 °C

Thickness of the BR Film	Original Weight of the Film	Weight of the Film After Desorption	Weight Loss	Equilibrium Concentration of the Penetrant C	Best Mean Value of C	Diffusion Coefficient $D_o \times 10^{12}$	Best Mean Value of $D_o \times 10^{12}$
mm	mg	mg	%	g/g	g/g	$m^2 s^{-1}$	$m^2 s^{-1}$
			GASOLINE				
0.11	68.0	63.0	7.35	0.715		0.787	
0.25	51.6	47.7	7.56	0.823		2.017	
0.25	55.0	49.6	9.82	0.830	0.817	2.788	2.155
0.34	64.4	59.0	8.40	0.900		3.027	
			TRICHLOROETHYLENE				
0.11	23.7	20.7	12.56	1.91		1.283	
0.11	48.4	43.4	10.33	1.97		1.228	
0.25	26.3	23.9	9.13	2.56	2.290	3.379	2.368
0.25	48.5	42.9	11.55	2.49		3.125	
0.34	48.3	44.7	7.45	2.52		2.826	
			AVIATION FUEL				
0.11	67.0	64.6	3.72	1.397		0.422	
0.11	43.5	39.7	8.08	1.471		0.190	
0.25	53.2	48.9	8.08	1.480	1.456	0.358	0.349
0.34	68.3	64.8	5.12	1.478		0.428	
			KEROSENE				
0.12	53.7	50.2	6.52	1.614		0.298	
0.12	24.9	22.5	9.638	1.634	1.624	0.187	0.242

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curves for polyisobutylene show no effect of film thickness on the vapour sorption of propane. This discrepancy may be due to the high uptake of liquid, heat of evaporation or due to the loss of weight by the rubber film. In our calculation of the mean diffusion coefficient, we have excluded the exceptionally odd values, so the mean value of D_o can be safely used.

The diffusivities of the penetrants studied follows the order: trichloroethylene > gasoline > aviation fuel > kerosene > diesel fuel. Since the exact composition of these fuels is not known, no theoretical justifications can be provided for this order. The diffusion coefficient of diesel fuel was extremely low and after long desorption time about 6% of the diesel fuel was still in the film, so strictly speaking, the D_o value reported for diesel fuel is not the diffusion coefficient at zero concentration. This also suggests that the sorption/desorption technique is not suitable for studying this type of penetrant. Nevertheless, we had been able to produce some reliable results for the other penetrants in a short time, which shows the usefulness of this technique.

(ii) Bromobutyl Rubber (BIIR)

Results for the diffusion of all the penetrants, except diesel fuel in bromobutyl rubber, are reported in Table 5.8. Due to the experimental difficulty mentioned earlier, we have excluded diesel fuel in this part of the study.

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TABLE 5.9

Comparison of the Diffusivities of Various Penetrants in Natural and Bromobutyl Rubbers

Penetrant	D_n/D_b Ratio
Gasoline	2.8
Kerosene	1.5
Aviation Fuel	15.1
Trichloroethylene	10.5

Compared to natural rubber the loss in the weight of the polymer film is higher, which suggests that the bromobutyl rubber has less "wetting" potential than natural rubber and there is a greater possibility for additives to ooze out in the solvent. The effect of the thickness of bromobutyl rubber films also seems to be less pronounced. Since the overall equilibrium uptake of the liquid is also lower than natural rubber, so perhaps the discrepancies in the value of diffusion coefficient arise from the assessment of equilibrium uptake.

The diffusivities of the penetrants in bromobutyl rubber are considerably lower than those in natural rubber. The double bond in a natural rubber molecule cases the segmentald rotation of the polymer chain, whereas the absence of such a bond and the presence of methyl and bromine in bromobutyl rubber may have a counter effect, so lower diffusivity in bromobutyl rubber can be expected. Table 3.1 shows similar behaviour of butyl rubber and natural rubber towards gases.

A quick comparison of the diffusivities of penetrants in both these rubbers can be made from the ratio of their diffusion coefficients, i.e., D_n/D_b, where D_n and D_b are the diffusion coefficients in natural and bromobutyl rubbers, respectively. These ratios are listed in Table 5.9. In the case of all solvents the ratio is high as expected, nevertheless, the exceptionally high values for the aviation fuel and trichloroethylene are worth noticing. We are not sure about the exact chemical composition of aviation fuel, but

the effect of chlorine is very obvious. Trichloroethylene diffusivity was higher in natural rubber, but its sudden drop in bromobutyl rubber may be the result of the halogenated backbone of the bromobutyl rubber. It is possible that the bromine and methyl group impede the mobility of this bulky chlorinated solvent, which was not the case in natural rubber. The effect is not very much evident with the hydrocarbon based fuels like gasoline. In one way, these findings can be reconciled with our data on polyethylene, where the size effect of chlorinated solvents is much more pronounced. Also, we can see from Table 3.1 that a halogenated rubber like polychloroprene has a lower diffusivity than its counterpart polybutadiene, so bromobutyl rubber shows the same trend in this work.

5.4. Theoretical Concentration-Time Profiles for the Penetration of Bis(2-Chloroethyl) Sulphide Through Slabs of Natural and Bromobutyl Rubbers

In order to calculate the concentration-time profiles we had to solve Fick's Second Law of Diffusion numerically for the case where the diffusion coefficient is dependent on concentration. Fick's Second Law is given by:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x}\right) \qquad (5.6)$$

Assuming that the diffusion coefficient, D, depends on

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concentration in the manner described by Equation (3.18), we wrote a computer programme (cf. Appendix A), which is capable of numerically solving the partial differential equation which results from substituting Equation (3.18), written in terms of diffusion coefficient, into Equation (5.6).

Before solving Fick's Second Law numerically, we had to rewrite the partial differential equation in a dimensionless form by utilizing the following:

dimensionless concentration = $C' = C/C_o$

dimensionless thickness = $x' = x/\ell$

dimensionless time = $t' = D_o\, t/\ell^2$

where C_o represents the initial concentration of the penetrant in the polymer and ℓ is the thickness of the polymer slab. Subtituting these dimensionless quantities into the partial differentiation equation yields:

$$\frac{\partial C'}{\partial t'} = \frac{\partial}{\partial x'}\left[(1-C'\,V_o)^2\,\mathrm{Exp}\{\frac{C'}{A+BC'}\}\,\frac{\partial C'}{\partial x'}\right] \qquad (5.7)$$

where

$$A = \frac{f(0,T)^2}{B_d\,\beta(T)V_o}$$

and

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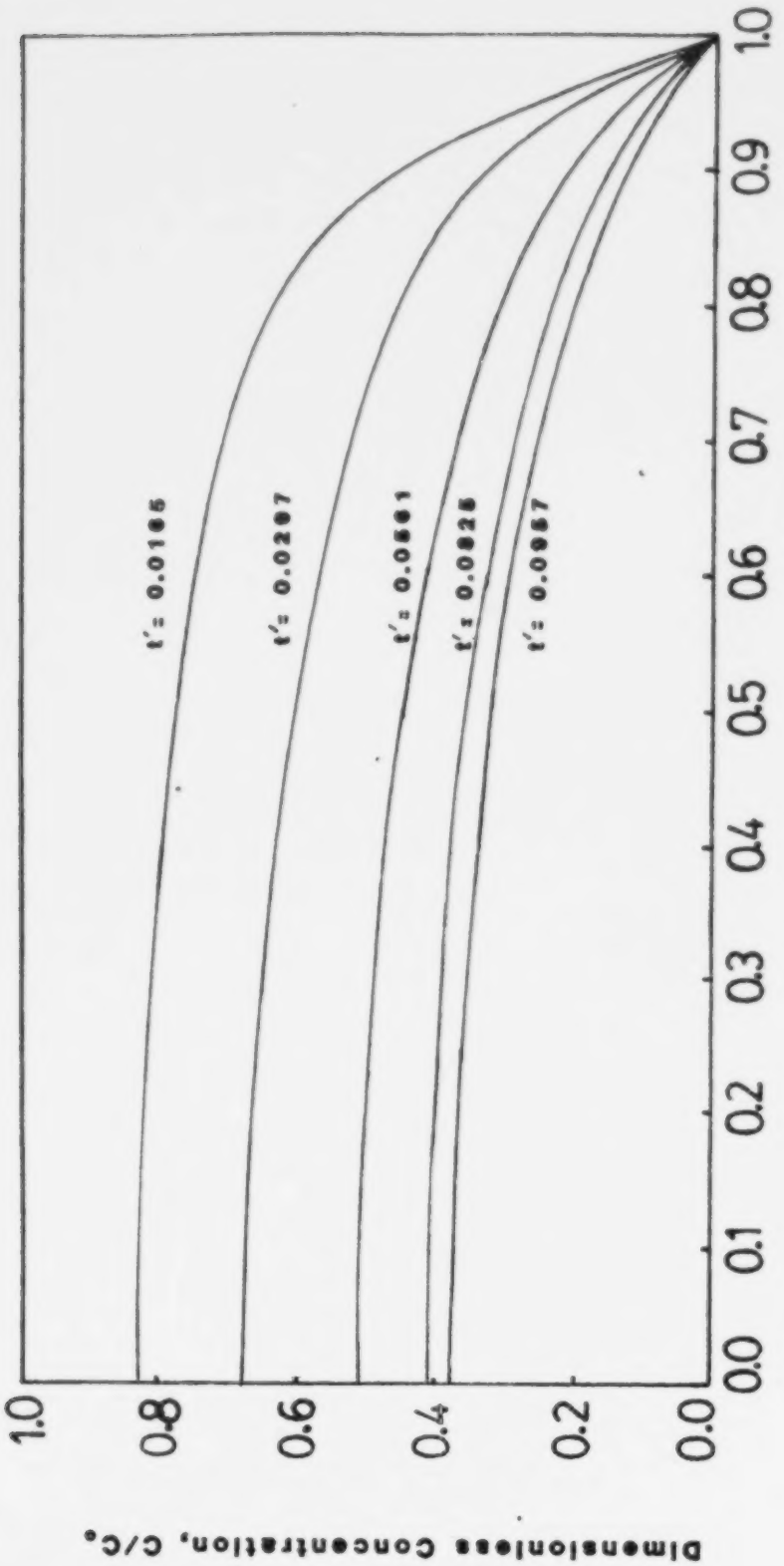

Figure 5.15- Theoretical Concentration-Time Profile for the System Natural Rubber-Bis(2-Chloroethyl) Sulphide

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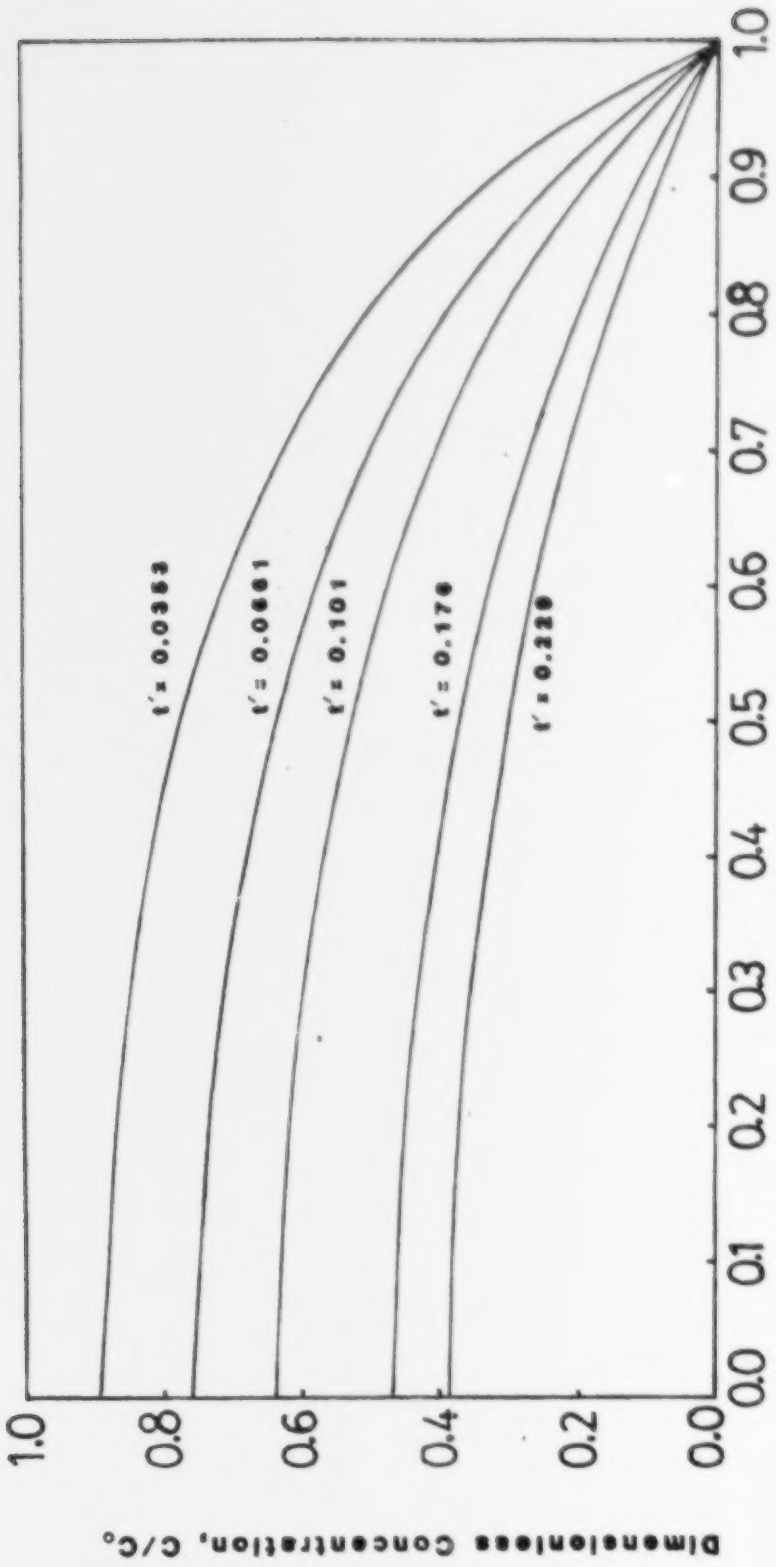

Figure 5.16- Theoretical Concentration-Time Profile for the System Bromobutyl Rubber-Bis(2-Chloroethyl) Sulphide

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$$B = \frac{f(0,T)^2}{B_d}$$

where $f(0,T)$ is the fractional free volume of the polymer, B_d is one of the free volume theory parameters [cf. Fujita 1960] and V_o is the equilibrium volume fraction of the liquid in the polymer.

Equation (5.7) was solved numerically to yield the dimensionless concentration-dimensionless time profiles. The computer programme used for this purpose is included in Appendix A along with the numerical values for the concentration-time profiles.

The theoretical concentration-time profiles for the case of natural rubber and bromobutyl rubbers are depicted in Figures 5.15 and 5.16. It should be noted here that at zero time the concentration profile is represented by a horizontal line since the slab is saturated with the penetrant. As soon as the vacuum is turned on, it is assumed that the surface concentration of the penetrant instantaneously drops to zero, which is a necessary condition for solving the partial differential equation. This assumption is a reasonable one, since practically as soon as the vacuum is turned on, the surface concentration of the penetrant immediately drops to a very small value which can be approximated to zero with a very small error.

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6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

Our diffusion studies on three polymers with a wide variety of penetrants enables us to draw the following conclusions:

(i) the desorption method is a useful technique for obtaining diffusion coefficients at zero penetrant concentration of small penetrant molecules and is free from the uncertainty which is inherent in the extrapolation techniques (e.g., sorption and time-lag methods). Consequently, the effect of temperature, polymer nature, size and shape of the penetrant molecule can easily be correlated with the diffusion coefficients,

(ii) the investigations on LDPE confirm that the diffusion coefficient decreases with increasing the size of the penetrant molecule. In the absence of shape effects a straight line relationship was found between log D_o and the molar volumes of the penetrants. When there is less fractional free volume in the polymer, either due to crystallinity or to the glassy nature of the polymer, this relationship between log D_o and molar volume holds well. This effect, however, may disappear once excess free volume

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becomes available. The shape of the penetrants has a profound effect on diffusion in polymers. The linear, flexible diffusant molecules diffuse more quickly than the rigid molecules irrespective of the nature of the polymer,

(iii) The magnitude of decrease of D_o with increasing the size of the penetrants follows the following order:

chlorinated solvents > hydrocarbons > benzenes.

This suggests that while comparing the effect of the size of the penetrants on diffusion, the molecular structure of the penetrants has to be taken into account. In one series of penetrants the length of the molecule may be controlling the rate of diffusion whereas the other, the diameter of the molecule, may play the dominant role,

(iv) the activation energy of diffusion also increases with increasing the molecular size, which may not be the case when relatively smaller size molecules are diffusing in rubbery polymers,

(v) semiquantitative estimates of free volume parameters for LDPE/penetrant systems suggest that the parameter B is a function of the size of the penetrant molecule and increases with increasing molecular size, whereas parameter A also shows an increase which, probably, is the result of crystallinity in LDPE

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(vi) investigation on rubbers show that the diffusivity of fuels, as well as the equilibrium uptake of these penetrants is higher in natural rubber compared with bromobutyl rubber

(vii) there is a sharp drop in the diffusivity of aviation fuel and trichloroethylene in bromobutyl rubber. This indicates that bromobutyl rubber is not only more resistant to ordinary fuel, but also its resistivity to chlorinated solvents is much higher than that of natural rubber,

(viii) the time-lag method which is employed by DREO for measuring diffusion coefficients is only reliable if the diffusion experiment is conducted long enough to reach steady state (cf. Equation 5.1). Attempting to use data in the unsteady state range to obtain diffusivity values can yield highly erroneous estimates for diffusivities. However, the desorption technique followed in this study takes much shorter times than the time-lag method and yields higher quality and reproducible data.

6.2. Recommendations

In the light of experience gained during this work we suggest the following points for future research in this field.

(i) considering the usefulness of the desorption method, the effect of the chemical nature of the polymer on diffusion can be easily studied by this method. The factors to be explored are, crystallinity, glass transition temperature, copolymers, polymer blends, and crosslinking in polymers. The experiments can be conducted over a range of temperatures, below and above the glass transition temperatures. This will enable us to establish the temperature dependence of the activation energy,

(ii) though the liquid sorption/desorption technique is useful in determining the influence of the above mentioned variables, however, it is cumbersome to evaluate the concentration dependence of diffusion coefficient by this method. On the other hand, the vapour sorption/desorption method enables one to evaluate concentration by a fairly established simple method. For this purpose, the same desorption apparatus can be used with some modifications for sorption studies.

(iii) time limitation did not allow us to investigate the effect of crosslinks and additives on diffusion in rubbers. Some work has been done so far as for diffusion of gases is concerned, but very little information is available for vapour sorption. The vapour sorption studies on vulcanized

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rubbers with additives of various natures should enable one to establish optimum composition of rubbers to resist a hostile environment.

(iv) this extensive work on the effect of size and shape of the penetrant molecule suggests that for the same chemical series of penetrants, fair predictions can be made about the diffusivity of lower and higher members of the series. For instance, the diffusivity of n-pentane and n-nonane can be fairly predicted from the extrapolation of Figure 5.10. Similarly, when the diffusivity of a chemically toxic compound is required, its analogous nontoxic compounds can be studied and then the diffusivity of the required compound can be worked out with fair certainty.

(v) when the time-lag method is used for measuring diffusion coefficients, enough time has to be allowed for reaching steady state. A reasonable estimate for such a time can be obtained from Equation (5.1).

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7. NOMENCLATURE

A = Free Volume Theory Pre-exponential Factor or β Particle Count

B = Free Volume Theory Constant

C = Concentration; moles/unit volume

c = concentration; mass/unit volume

D = Diffusion Coefficients; m^2/s

E = Activation Energy; kJ/mol

F = Flux; moles/unit area x unit time

f = fractional Free Volume

L = Time Lag

ℓ = Film Thickness; m or mm

M = Mass; kg or gm

P = Permeability Coefficient

R = Universal Gas Constant

s = Solubility

T = Temperature; K

t = Time; seconds

V = Molar Volume; m^3/kmol or L/kmol

v = Specific Volume; m^2/kg or L/gm

Superscripts

* = Thermodynamic

C = Co-ordinate-Fixed Frame of Reference

v = Volume-Fixed Frame of Reference

Subscripts

o, ∞ = Initial and at infinite time, respectively

A, B = Components in a Mixture

d = Diffusion

e = Equilibrium

g = Glass Transition

i = Intrinsic or Component i

t = Time

Greek Letters

α = Thermal Expansion Coefficient or Constant

β' = Thermodynamic Correction Factor

β'' = Parameter Representing the Contribution of Penetrant to the Free Volume

ϕ = Volume Fraction of Penetrant

ς = Quantity Defined by Equation (3.24)

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8. REFERENCES

Alfrey, T., Gurnee, E.F., and Lloyd, W.G. [1966] "Diffusion in Glassy Polymers", J. Polym. Sci., C12, 249.

Amerongen Van, G.J. [1946] "The Permeability of Different Rubbers to Gases and Its Relation to Diffusivity and Solubility", J. Appl. Polym. Sci., 17, 927.

Amerongen Van, G.J. [1947] "Solubility, Diffusion, and Permeation of Gases in Gutta-Percha", J. Polym. Sci., 2, 381.

Amerongen Van, G.J. [1950] "Influence of Structure of Elastomers on Their Permeability to Gases", J. Polym. Sci., 5, 307.

Amerongen Van, G.J. [1955] "The Effect of Fillers on the Permeability of Rubber to Gases", Rubber Chem. and Technol., 28, 821.

Amerongen Van, G.J. [1964] "Diffusion in Elastomers", Rubber Chem. and Technol., 37, 1065.

Araimo, L., DeCandia, F., Vittoria, V. and Peterlin, A. [1978] "Mechanical and Transport Properties", J. Polym. Sci., 16, 2087.

Asfour, Abdul-Fattah A. [1979] Ph.D. Thesis, University of Waterloo, Waterloo, Ontario, Canada.

Asfour, Abdul-Fattah A., D.C.R. De Kee and M.G. Zedan. [1984] Unpublished work.

Aitken, A. and Barrer, R.M. [1955] "Transport and Solubility of Isomeric Paraffins in Rubber", Trans. Faraday. Soc., 51, 116.

Baddour, R.F., Michaels, A.S., Bixler, H.J., DeFilippi, R.P. and Barrie, J.A. [1964] "Transport of Liquid in Structurally Modified Polyethylene", J. Appl. Polym. Sci., 8, 897.

Bagley, E. and Long, F.A. [1955] "Two-Stage Sorption aand Desorption of Organic Vapors in Cellulose Acetate", J. Am. Chem. Soc., 77, 2172.

Barrer, R.M. [1941] "Diffusion In and Through Solids", Cambridge University Press, London.

Barrer, R.M. [1957] "Properties of Diffusion Coefficients in Polymers", J. Phys. Chem. Wash., 61, 178.

Barrer, R.M., Barrie, J.A. and Rogers, M.G. [1963] "Heterogeneous Membranes: Diffusion in Filled Rubber", J. Polym. Sci., A1, 2565.

Barrer, R.M., Barrie, J.A. and Wong, P.S.L. [1968] "The Diffusion and

P148549.PDF [Page: 113 of 137]

Solution of Gases in Highly Crosslinked Copolymers", Polymer, 9, 609.

Barrer, R.M. and Chio, H.T. [1965] "Solution and Diffusion of Gases and Vapors in Silicone Rubber Membranes", J. Polym. Sci., C10, 111.

Barrer, R.M. and Skirrow, G. [1948] "Transport and Equilibrium Phenomena in Gas-Elastomer Systems. I. Kinetic Phenomena", J. Polym. Sci., 3, 549.

Bearman, R.J. [1961] "On the Molecular Basis of Some Current Theories of Diffusion", J. Phys. Chem., 66, 2699.

Berens, A.R. [1982] "Diffusion of Organic Vapors at Low Concentrations in Glassy PVC, Polystyrene and PMMA", J. Memb. Sci., 10, 285.

Bischoff, M. and Eyerer, P. [1984] "Growth of the Polarization Lay r in Ultrafiltration with Hollowfibre Membranes", J. Memb. Sci., 21, 333.

Blackadder, D.A. and Keniry, J.S. [1974] "Difficulties Associated with the Measurement of the Diffusion Coefficient of Solvating Liquid or Vapor in Semicrystalline Polymer. II. Sorption-Desorption Kinetics", J. Appl. Polym. Sci., 18(3), 699.

Brandt, W.W. [1959] "Model Calculation of the Temperature Dependence of Small-Molecule Diffusion in High Polymers", J. Phys. Chem. Wash., 63, 1080.

Brown, W.R. and Park, G.S. [1970] "Diffusion of Solvent and Swellers in Polymers", J. Paint. Technol., 42, 16.

Brown, W.R., Jenkins, R.B. and Park, G.S. [1973] "Sorption and Diffusion of Small Molecules in Amorphous and Crystalline Polybutadienes", J. Polym. Sci., Polym. Symp., 41, 45.

Bueche, F. [1953] "Segmental Mobility of Polymers Near Their Glass Temperature", J. Chem. Phys., 21, 1850.

Cohen, M.H. and Turnbull, D. [1959] "Molecular Transport in Liquids and Glasses", J. Chem. Phys., 31, 1164.

Crank, J. [1953] "A Theoretical Investigation of the Influence of Molecular Relaxation and Internal Stress on Diffusion in Polymers", J. of Polym. Sci., 11, 151.

Crank, J. [1956] "Some Methods of Deducing the Diffusion Coefficient and its Concentration Dependence from Sorption Experiments", Trans. Faraday Soc., 51 1632.

Crank, J. [1979] "The Mathematics of Diffusion", 2nd Edition, Clarendon Press, Oxford.

Crank, J. and Park, G.S.[1949] "An Evaluation of the Diffusion

Coefficient for Chloroform in Polystyrene from Simple Absorption Experiments", Trans. Faraday. Soc., 45, 240.

Crank, J. and Park, G.S. [1951] "Diffusion in High Polymers: Some Anomalies and Their Significance", Trans. Faraday Soc., 47, 1072.

Crank, J. and Park., G.S., Eds. [1968] "Diffusion in Polymers", Academic Press, New York.

Crank, J. and Robinson, C. [1951] "Interferometric Studies in Diffusion. II. Influence of Concentration and Orientation on Diffusion in Cellulose Acetate", Proc. Royal Soc., A204, 549.

Crank, J. [1979] "The Mathematics of Diffusion", 2nd Edition, Clarendon Press, Oxford.

Cohen, M.H. and Turnbull, D. [1959] "Molecular Transport in Liquids and Glasses", J. Chem. Phys., 31, 1164.

Cullinan, H.T. and Lenczyk, J.P. [1969] "Determination of Chemical Potential Composition of Derivatives by Equilibrium Sedimentation", Ind. Eng. Chem., Fundamentals, 8, 819.

Dankwerts, P.V. [1971] "Diffusion and Mass Transfer in Diffusion Processes", Sherwood, J.N., A.V. Chadwick, W.M. Muir, and F.L. Swinton, (Eds.), 2, 545, Gordon and Breach, New York.

Darken, L.S. [1949] "Diffusion, Mobility and Their Interrelation Through Free Energy in Binary Metallic Systems", Trans. Am. Inst. Mining Met. Eng., 175, 184.

Dayness, H.A. [1920] "The Process of Diffusion Through a Rubber Membrane", Proct. R. Soc., A97, 286.

DeCandia, F., Russo, R., Vittoria, V. and Peterlin, A. [1980] "Transport Properties of Annealed Drawn Low-Density Polyethylene (LDPE)", Journal of Polymer Science, Phys. Ed., 18, 2083.

DeCandia, F., Russo, R. and Vittoria, A. [1982] "Mechanical and Transport Properties of Drawn Crosslinked Low-Density Polyethylene", J. Polym. Sci., Phys. Ed., 20, 269.

Drechsel, P., Hoard, J.L. and Long, F.A. [1953] "Diffusion of Acetone into Cellulose Nitrate Films and Study of the Accompanying Orientation", J. Polym. Sci., 10, 241.

Duda, J.L., Vrentas, J.S., Ju, S.T. and Liu, H.T. [1982] "Prediction of Diffusion Coefficient for Polymer-Solvent Systems", AIChE J., 28(2), 27.

Dullien, F.A.L. [1960] Ph.D. Thesis, University of British Columbia, British Columbia, Canada.

P148549.PDF [Page: 115 of 137]

Dullien, F.A.L. [1979] "Diffusion in Isotropic Mixtures", unpublished work.

Dullien, F.A.L. and Asfour, A.A. [1985] "Concentration Dependence of Mutual Diffusion Coefficients in Regular Binary Solution: A New Predictive Equation", I&EC Fundamentals, 24, 1.

Fels, M. and Li, N.N. [1974], in "Permeability of Plastic Films and Coatings", Hopfenburg, H.P.,Editor, Plenum Press, New York, 357.

Fleischer, G. [1985] "The Diffusion of Benzene-Cyclohexane and Benzene Toluene Mixtures in Polyethylene Using the Pulsed Field Gradient NMR Technique", Polym. Commun., 26, 20.

Fujita, H., Kishimoto, A. and Matsumoto, K. [1960] "Concentration and Temperature Dependence of Diffusion Coefficients for Systems Polymethyl Acrylate and n-Alkyl Acetate", Trans. Faraday Soc., 56, 424.

Fujita, H. [1961] "Diffusion in Polymer-Diluent Systems", Fortschr. Hochopolymer. Forsch., 3, 1.

Garret, A.T. [1965], M.Sc. Thesis, University of Wales, United Kingdom.

Ghai, R.K., Erti, H. and Dullien, F.A.L. [1973] "Liquid Diffusion of Nonelectrolytes: Part I", AIChE J., 19, 881.

Gordan, M. (Editor) [1985], "Polymer Membranes", Springer-Verlag, Heidelberg.

Gray, A. and Gilbert, M. [1975] "Solvent Sorption of Heat Treaated Vinyl Chloride Polymers", Polymer, 16, 387.

Gregg, S.J. [1961] "The Surface Chemistry of Solids", Chapman and Hall, London.

Hartley, G.S. and Crank, J. [1949] "Some Fundamental Definitions and Concepts in Diffusion Process", Transaction of Faraday Society, 45, 801.

Hayes, M.J. and Park, G.S. [1955] "The Diffusion of Benzene in Rubber. Part I: Low Concentrations of Benzene", Trans. Faraday Soc., 51, 1134.

Hopfenberg, H.B., Holley, R.H. and Stannet, V. [1969] "Effect of Penetrant Activity and Temperature on the Anomalous Diffusion of Hydrocarbons and Solvent Crazing in Polystyrene. I. Biaxially-Oriented Polystyrene", J. Polym. Sci. 9, 242.

Hofenberg, H.B., Holley, R.H. and Stannet, V.T. [1970] "Anomalous Transport of Hydrocarbons in Polystyrene", Poly. Eng. Sci., 10, 376.

1/2 N6

Hopfenberg, H.B. (Editor) [1974] "Permeability of Plastic Films and Coatings", Plenum Press, New York.

Jenkins, R.B. [1976] Ph.D. Thesis, University of Wales, United Kingdom.

Ju, S.T., Liu, H.T., Duda, J.L. and Vrentas, J.S..[1981] 'Solvent Diffusion in Amorphous Polymers", J. Appl. Polym. Sci., 26, 3735.

Jurbak, A.F. (Editor) [1981] "Symmetric Membranes", Vol. I-II, Am. Chem. Soc., Washington, D.C.

Kesting, P.E. (Editor) [1971] "Synthetic Polymeric Membranes", McGraw-Hill, New York.

King, G. and Cassie, A.B.D. [1940] "Propagation of Temperature Changes Through Textiles in Humid Atmosphere. Part I. Rate of Absorption of Water Vapour by Wool Fibres", Trans. Faraday Soc., 36, 445.

Kokes, R.J. and Long, F.A. [1953] "Diffusion of Organic Vapors into Polyvinyl Acetate", J. Am. Chem. Soc., 75, 6142.

Kovacs, A. [1948] "Diffusion and Absorption of Water in Plastic Materials", J. Chem. Phys.j, 45, 258.

Kreituss, A. and Frisch, H.L. [1981] "Free-Volume Estimates in Heterogenous Polymer Systems", J. Polym. Sci., 19, 889.

Kumins, C.A. and Roteman, J. [1961] "Diffusion of Gases and Vapors Through Polyvinyl Chloride-Polyvinyl Acetate Copolymer Films. I. Glass Transition Effect", J. Polym. Sci., 55, 683.

Kwei, T.K. and Zupko, H.M. [1969] "Diffusion in Glassy Polymers. I.", J. Polym. Sci., (A2), 7, 867.

Li, N.N., Long, R.B. and Henly, E.J. [1965] "Membrane Separation Process", Ind. Eng. Chem., 57(3), 18.

Long, F.A. and Wilkins, J.B. [1957] "A Free-Volume Model for Diffusion of Small Molecules in Polymers. (Abstract)", Trans. Faraday Soc., 53, 1146.

Manaresi, P. and Giannella, V. [1960] "Second Order Transition Temperature of Ethylene-Propylene Copolymers", J. Appl. Polym. Sci., 4, 251.

McCall, D.W., Douglas, D.C., Bair, H.E., Johnson, Eds., G., Blyler, L.L. and Jelinski, L.W. [1984] "Solubility and Diffusion Water in Low-Density Polyethylene in Macromolecules", 17, 1644.

Meares, P. [1954] "The Diffusion of Gases Through Polyvinyl Acetate", J. Am. Chem. Soc., 76, 3415.

Meares, P. [1957] "The Diffusion of Gases in Polyvinyl Acetate in Relation to the Second Order Transition", Trans. Faraday Soc., 53, 101.

Meares, P. [1958] "Diffusion of Allyl Chloride in Polyvinyl Acetate. Part I. The Steady State of Permeation", J. Polym. Sci., 27, 391.

Michaels, Alan S., Baddour, Raymond F., Bixler, Harris J. and Choo, C.Y. [1962] "Conditioned Polyethylene as a Permselective Membrane", I&EC, Proc. Des. Dev., 1, 14-25.

Michaels, A.S. and Bixler, H.J. [1961] "Flow of Gases Through Polyethylene", J. Polym. Sci., 50, 413.

Michaels, A.S. and Parker, R.B. [1959] "Sorption and Flow of Gases in Polyethylene", J. Polym. Sci., 41, 53.

Moore, R.S. and Ferry, J.D. [1962] "Diffusion of Radioactively Tagged Cetane in Polyisobutylene-Cetane Mixtures and in Three Methacrylate Polymers", J. Phys. Chem., 66, 2699.

Mozisec, M. [1971] "The Diffusion of Solvents in Various Types of Rubber", J. Inst. Rubb. Ind., 5, 31.

Ng, H.C., Leung, W.P. and Choy, C.L. [1985] "Sorption and Diffusion of Toluene in Isotropic and Oriented Linear Polyethylene", J. Polym. Sci. Phys. Ed., 23, 973.

Nicolais, L., Apicella, A., Drioli, E. and Hofenberg, H.B. [1979] "Effect of Orientation on the Penetration Crazing and Dissolution of Polystyrene by n-Hexane", Polymer, 20, 459.

Nicolais, L. and Apicella A. DeNotaristefano [1984] "Time-Temperature Superposition of n-Hexane Sorption in Polystyrene", Journal of Membrane Science, 18, 187.

Park, G.S. [1950] "The Diffusion of Some Halo-Membranes in Polystyrene", Trans. Faraday Soc., 46, 684.

Park, G.S. [1968] "The Glassy State and Slow Process Anomalies in Diffusion in Polymers", Crank, J. and Park, G.S., Eds., Academic Press, New York.

Park, G.S. and Saleem, M. [1984] "Diffusion of Additives and Plasticizers in Poly(vinyl chloride)-V. Diffusion of n-Hexadecane and DDT in Various Poly(vinyl chloride)/Dialkylphthalate Compositions", J. Memb. Sci., 18, 177.

Park, G.S. and Said, M.M. [1985] "Some Aspects of Diffusion in Cellulose Nitrate".

Park, G.S. and Saleem, M. [1985] "The Sorption and Diffusion of Organic Vapours in Plasticized PVC", International Conference on

P148549.PDF [Page: 118 of 137]

Diffusion in Polymers, London, United Kingdom.

Paul, C.W. [1983] "A Model for Predicting Solvent Self-Diffusion Coefficients in Nonglassy Polymer/Solvent Solutions", J. Polym. Sci., Phys. Ed., 21, 425.

Prager, S. and Long, F.A. [1951] "Diffusion of Hydrocarbons in Polyisobutylene", J. Am. Chem. Soc., 73, 4072.

Pragers, S., Bagley, E. and Long, F.A. [1953] "Diffusion of Hydrocarbon Vapors into Polyisobutylene II", J. Am. Chem. Soc., 75, 1255.

Rembannes, A. and Shen, M. (Editors) [1971] "Biomedical Polymers", Marcel Dekker, New York.

Roger, C.E., Stannet, V. and Szwarc, M. [1960] "The Sorption Diffusion, and Permeation of Organic Vapors in Polyethylene", J. Polym. Sci. 45, 61.

Rosen, B. [1959] "A Recording Sorption Kinetics Apparatus", J. Polym. Sci., 35, 335.

Saleem, M. [1977] Ph.D. Thesis, University of Wales, United Kingdom.

Saleem, M., Asfour, Abdul-Fattah A., De Kee, D. and Harrison, B. [1986], "Diffusion of Saturated Hydrocarbons in Low Density Poly(ethylene) (LDPE) Films", J. of Membrane Sci. (accepted).

Sefcik, M.D., Schaefer, J., May, F.L., Rancher, D. and Dub, S.M. [1983] "Diffusivity of Gases and Main-Chain Cooperative Motions in Plasticized Poly(vinyl chloride)", J. Polym. Sci., Polym. Phys. Ed., 21, 1054.

Skirrow, G. and Young, K.R. [1974] "Sorption, Diffusion, and Conduction in Polyamide-Penetrant Systems. 1. Sorption Phenomena", Polymer, 15, 771.

Stannet, V. and Williams, J.L. [1966] "The Permeability of Poly(ethyl methacrylate) to Gases and Water Vapor", J. Polym. Sci., 10, 45.

Stober, E.J., Seferic, J.C. and Kennan, J.D. [1984] "Characterization and Exposure of Polyetherketone Fluid Environments", Polymer, 25, 1845.

Thomas, N.L. and Windle, A.H. [1981] "Diffusion Mechanics of the System PMMA-Methanol", Polymer, 22, 627.

Thomas, N.L. and Windle, A.H. [1982] "A Theory of Case II Diffusion", Polymer, 23, 529.

Turbak, Albin F. [1981] "Synthetic Membranes", ACS Symposium Series, Volumes 153 and 154.

Tyrrel, H.J.V. [1969] "Diffusion in Liquids in Diffusion Processes", Vol. 1, Chapter 2 (Eds.) Sherwood, J.N., Chadwick, A.V., Muir, W.M. and Swinton, F.L., Gordon and Breach Science Publishers, New York.

Vieth, W.R., Douglas, A.S. and Block, R. [1969] "Membrane-Water Structural Interaction in Reverse Osmosis Transport", J. Macromol. Sci. Phys., B3, 737.

Vrentas, J.S. and Duda, J.L. [1977] "Diffusion in Polymer-Solvent Systems. I. Reexamination of the Free-Volume Theory", J. Polym. Sci., Phys. Ed., 15, 403.

Vrentas, J.S. and Duda, J.L. [1979] "Molecular Diffusion in Polymer Solutions", AIChE J., 25, 1.

Vrentas, J.S., Duda, J.L. and Ling, H.C. [1985a] "Free-Volume Theories for Self-Diffusion in Polymer Solvent Systems. I. Conceptual Differences in Theories", J. Polym. Sci.,. Phys. Ed., 23, 275.

Vrentas, J.S., Duda, J.L. and Ling, H.C. [1985b], "The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-Forming Liquids", J. Am. Chem. Soc., 77, 3701.

Williams, M.L., Landel, R.F. and Ferry, J.D. [1955], "Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-Forming Liquids", J. Am. Chem. Soc., 77, 3701.

APPENDICES

APPENDIX A

- Computer Program, which can be run on an IBM-XT microcomputer, for the calculation of the theoretical concentration-time profiles.

- Theoretical concentration-time profiles calculated for:
  (i) Natural Rubber-Bis(2-Chloroethyl) Sulphide System
  (ii) Bromobutyl Rubber-Bis(2-Chloroethyl) Sulphide System.

```
$DEBUG                                                                  FEL00010
      REAL AP(21),AM(21),AS(21),BP(21),C(21),CO(21),X(21)               FEL00040
      REAL QEXP(100),QI(100),E(100),DTT(100)                            FEL00050
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCFEL00080
C     IDENTIFICATION                                                    FEL00090
      OPEN ( 3,FILE='FELS.DAT')                                         FEL00100
      OPEN ( 2,FILE='OUT02.DAT',STATUS='NEW')                           FEL00110
      OPEN ( 4,FILE='OUT04.DAT',STATUS='NEW')                           FEL00120
      OPEN (20,FILE='OUT20.DAT',STATUS='NEW')                           FEL00110
      OPEN (21,FILE='OUT21.DAT',STATUS='NEW')                           FEL00120
      OPEN (30,FILE='OUT30.DAT',STATUS='NEW')                           FEL00110
      OPEN (31,FILE='OUT31.DAT',STATUS='NEW')                           FEL00120
      OPEN (32,FILE='OUT32.DAT',STATUS='NEW')                           FEL00110
      OPEN (33,FILE='OUT33.DAT',STATUS='NEW')                           FEL00120
      OPEN (34,FILE='OUT34.DAT',STATUS='NEW')                           FEL00110
      OPEN (35,FILE='OUT35.DAT',STATUS='NEW')                           FEL00120
      OPEN (36,FILE='OUT36.DAT',STATUS='NEW')                           FEL00110
      OPEN (37,FILE='OUT37.DAT',STATUS='NEW')                           FEL00120
      OPEN (38,FILE='OUT38.DAT',STATUS='NEW')                           FEL00110
      OPEN (39,FILE='OUT39.DAT',STATUS='NEW')                           FEL00120
      OPEN (40,FILE='OUT40.DAT',STATUS='NEW')                           FEL00110
      OPEN (41,FILE='OUT41.DAT',STATUS='NEW')                           FEL00120
      OPEN (42,FILE='OUT42.DAT',STATUS='NEW')                           FEL00110
      OPEN (43,FILE='OUT43.DAT',STATUS='NEW')                           FEL00120
      IOFILE=4                                                          FEL00140
      IOUT=2                                                            FEL00150
      INFILE=3                                                          FEL00160
      IINPUT=3                                                          FEL00170
      WRITE(*,*)'                                                      '
      WRITE(*,*)'   '
      WRITE(*,*)'   '
      WRITE(*,*)'   '
      WRITE(*,*)' ::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::'
      WRITE(*,*)' ::                                                              ::'
      WRITE(*,*)' ::                                                              ::'
      WRITE(*,*)' ::  D I F F U S I O N   I N   P O L Y M E R S                   ::'
      WRITE(*,*)' ::                                                              ::'
      WRITE(*,*)' ::                      F O R                                   ::'
      WRITE(*,*)' ::                                                              ::'
      WRITE(*,*)' ::1.Concentration Profiles in Thin Polymer Films                ::'
      WRITE(*,*)' ::                                                              ::'
      WRITE(*,*)' ::2.Free_Volume Theory Parameters                               ::'
      WRITE(*,*)' ::                                                              ::'
      WRITE(*,*)' ::                      B Y                                     ::'
      WRITE(*,*)' ::                                                              ::'
      WRITE(*,*)' ::            Dr. A. A S F O U R                                ::'
      WRITE(*,*)' ::                                                              ::'
      WRITE(*,*)' ::            CHEMICAL ENGING. DEPT.                            ::'
      WRITE(*,*)' ::                                                              ::'
      WRITE(*,*)' ::            UNIVERSITY OF WINDSOR                             ::'
      WRITE(*,*)' ::                                                              ::'
      WRITE(*,*)' ::                  1 9 8 6                                     ::'
      WRITE(*,*)' ::                                                              ::'
      WRITE(*,*)' ::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::'
```

```
      PAUSE
C                                                                       FEL00180
C ----INPUT DATA                                                        FEL00190
C                                                                       FEL00200
      READ (IINPUT,200) THICK,DCO,VO,DTMAX                              FEL00210
      READ (IINPUT,201) A,B                                             FEL00220
      WRITE(*,*)'          '
      WRITE(*,*)'         THE INITIAL VALUE OF ( A )  AND ( B )  ARE :'
      WRITE(*,*)'          '
      WRITE(*,*) A,B
      WRITE(*,*)'    '
      WRITE(*,*)'         CHANGE THE CURRENT INITIAL VALUES  (Y/N)   ?'
      READ(*,'(A)') FLAG
      IF (FLAG.EQ.'N'.OR.FLAG.EQ.'n') GO TO 1001
      WRITE(*,*)'      '
      WRITE(*,*)'        ENTER NEW INITIAL VALUE FOR  A AND  B  ----->'
      READ(*,*) A,B
1001  READ (IINPUT,201) PDA,PDB                                         FEL00230
      READ (IINPUT,201) PDELTA,PDELTB                                   FEL00240
      READ (IINPUT,203) ITMAX,ILMAX,JLMAX,INTLPM                        FEL00250
      WRITE(*,*)'          '
      WRITE(*,*)'         THE NUMBER OF ITERATIONS TO GET  A&B   ARE :'
      WRITE(*,*)'          '
      WRITE(*,*)ILMAX,JLMAX
      WRITE(*,*)'          '
      WRITE(*,*)'         CHANGE THE CURRENT ITERATION NUMBER (Y/N)  ?'
      READ(*,'(A)') FLAG
      IF (FLAG.EQ.'N'.OR.FLAG.EQ.'n') GO TO 1002
      WRITE(*,*)'      '
      WRITE(*,*)'        ENTER NEW VALUE FOR  ILMAX AND JLMAX  ----->'
      READ(*,*) ILMAX,JLMAX
1002  READ (IINPUT,204) ICOFPR,ICONPR,IQIPR,IERPR,IPLOT                 FEL00260
      WRITE(*,*)'          '
      WRITE(*,*)'         THE CONTROL PARAMETERS FOR THE OUTPUT  ARE :'
      WRITE(*,*)'INTLPM,ICOFPR,ICONPR,IQIPR,IERPR,IPLOT    '
      WRITE(*,*) INTLPM,ICOFPR,ICONPR,IQIPR,IERPR,IPLOT
      WRITE(*,*)'          '
      WRITE(*,*)'         CHANGE THE CURRENT OUTPUT PARAMETERS(Y/N)  ?'
      READ(*,'(A)') FLAG
      IF (FLAG.EQ.'N'.OR.FLAG.EQ.'n') GO TO 1003
      WRITE(*,*)'      '
      WRITE(*,*)'        ENTER NEW VALUE FOR OUTPUT PARAMETERS ----->'
      READ(*,*) INTLPM,ICOFPR,ICONPR,IQIPR,IERPR,IPLOT
```

```
1003  WRITE(*,*)'   '
      WRITE(*,*)' ::::::::::::::::::::::::::::::::::::::::::::::::::::::::'
      WRITE(*,*)' ::                                                    ::'
      WRITE(*,*)' ::                                                    ::'
      WRITE(*,*)' ::     B E     P A T I E N T     W A I T              ::'
      WRITE(*,*)' ::                                                    ::'
      WRITE(*,*)' ::                                                    ::'
      WRITE(*,*)' ::                    F O R                           ::'
      WRITE(*,*)' ::                                                    ::'
      WRITE(*,*)' ::                                                    ::'
      WRITE(*,*)' ::         T H E   P R O M P T   ( > )                ::'
      WRITE(*,*)' ::                                                    ::'
      WRITE(*,*)' ::                                                    ::'
      WRITE(*,*)' ::                                                    ::'
      WRITE(*,*)' ::     THE RESULTS WILL BE STORED IN FILES            ::'
      WRITE(*,*)' ::                                                    ::'
      WRITE(*,*)' ::      OUT02.DAT, OUT04.DAT AND OUT*.DAT             ::'
      WRITE(*,*)' ::                                                    ::'
      WRITE(*,*)' ::::::::::::::::::::::::::::::::::::::::::::::::::::::::'
      WRITE(*,*)'   '
  200 FORMAT (F10.6/E14.6/F10.6/F10.6)                                  FEL00270
  201 FORMAT (F10.6/F10.6)                                              FEL00280
  203 FORMAT (I5/I5/I5/I5)                                              FEL00290
  204 FORMAT (I5/I5/I5/I5/I5)                                           FEL00300
C                                                                       FEL00310
C----- GRID SIZE                                                        FEL00320
C                                                                       FEL00330
      NJ=11                                                             FEL00340
      JD=21                                                             FEL00350
      MPD=100                                                           FEL00360
      JB=2                                                              FEL00370
      JE=NJ-1                                                           FEL00380
      JEP1=JE+1                                                         FEL00390
      DX=1./(NJ-1)                                                      FEL00400
      X(1)=0.0                                                          FEL00410
      DO 1 J=2,NJ                                                       FEL00420
      X(J)=X(J-1)+DX                                                    FEL00430
    1 CONTINUE                                                          FEL00440
C                                                                       FEL00450
C ---- READ QEXP FORM THE INPUT FILE                                    FEL00460
C                                                                       FEL00470
      IF (ITMAX.LT.100) GO TO 5                                         FEL00480
      IF (MOD(ITMAX,2).EQ.0) GO TO 5                                    FEL00490
      WRITE (IOFILE,7)                                                  FEL00500
    7 FORMAT (///,'**** WRONG INPUT DATA FOR ITMAX (IT SHOULD BE        FEL00510
     K        AN ODD NUMBER), OR ITMAX SHOULD NOT BE MORE THAN 100 ***' FEL00520
     K        ,///)                                                     FEL00530
      STOP                                                              FEL00540
    5 CONTINUE                                                          FEL00550
```

```
C                                                                       FEL00560
      DO 9 IT=1,ITMAX                                                   FEL00570
      READ (INFILE,11) DTT(IT),QEXP(IT)                                 FEL00580
    9 CONTINUE                                                          FEL00590
   11 FORMAT (E14.6,2X,E14.6)                                           FEL00600
C                                                                       FEL00610
C---- ECHO DATA                                                        FEL00620
C                                                                       FEL00630
      WRITE (IOFILE,207) THICK,DCO,VO,DTMAX                             FEL00640
      WRITE (IOFILE,208) A,B                                            FEL00650
      WRITE (IOFILE,209) PDA,PDB                                        FEL00660
      WRITE (IOFILE,210) PDELTA,PDELTB                                  FEL00670
      WRITE (IOFILE,211) NJ,JD                                          FEL00680
      WRITE (IOFILE,212) ITMAX,ILMAX,JLMAX,INTLPM                       FEL00690
      WRITE (IOFILE,213) ICOFPR,ICONPR,IQIPR,IERPR,IPLOT                FEL00700
      WRITE (IOFILE,214)                                                FEL00710
  207 FORMAT (/,5X,'POLYMER  PARAMETERS',/,5X,19(1H=),/                 FEL00720
     K          ,5X,'L THICK. CM =',F10.6,/                           FEL00730
     K          ,5X,'DCO CM.CM/S =',E14.6,/                           FEL00740
     K          ,5X,'   VO       =',F10.6,/                           FEL00750
     K          ,5X,' MAX. DT    =',F10.6)                            FEL00760
  208 FORMAT (5X,'INTIAL A    =',E14.6,/                              FEL00770
     K       ,5X,'INTIAL B    =',E14.6)                              FEL00780
  209 FORMAT (5X,'PER. DA     =',F10.6,/                              FEL00790
     K       ,5X,'PER. DB     =',F10.6)                              FEL00800
  210 FORMAT (5X,'PER. DELTA  =',F10.6,/                              FEL00810
     K       ,5X,'PER. DELTB  =',F10.6)                             FEL00820
  211 FORMAT (/,5X,'GRID PARAMETERS',/,5X,15(1H=),/                   FEL00830
     K          ,5X,'NUMBER OF GRID IN X DIRECTION =',I5,/           FEL00840
     K          ,5X,'MAXIMUM NUMBER OF GRID        =',I5)            FEL00850
  212 FORMAT (/,5X,'CONTROL PARAMETERS',/,5X,17(1H=),/                FEL00860
     K          ,5X,'MAXIMUM NUMBER OF QEXP POINT        =',I5,/     FEL00870
     K          ,5X,'MAX.NO. OF LOOP FOR A               =',I5,/     FEL00880
     K          ,5X,'MAX.NO. OF LOOP FOR B               =',I5,/     FEL00890
     K          ,5X,'MAXIMUM NUMBER OF INNER LOOP        =',I5)      FEL00900
  213 FORMAT (/,5X,'CONTROL OUTPUT PARAMETERS',/,5X,25(1H=),/         FEL00910
     K         ,5X,'     COEFFICIENT  OUTPUT C.P.       =',I5,/     FEL00920
     K         ,5X,'   CONCENTRATION  OUTPUT C.P.       =',I5,/     FEL00930
     K         ,5X,'              QI   OUTPUT C.P.       =',I5,/     FEL00940
     K         ,5X,'     COEFFIERROR  OUTPUT C.P.       =',I5,/     FEL00950
     K         ,5X,'        PLOTTING  OUTPUT C.P.       =',I5)      FEL00960
  214 FORMAT (//,10X,'DTT(IT)',10X,'QEXP(IT)',/)                      FEL00970
      DO 215 IT=1,ITMAX                                               FEL00980
      WRITE (IOFILE,216) DTT(IT),QEXP(IT)                             FEL00990
  215 CONTINUE                                                        FEL01000
  216 FORMAT (5X,E14.6,10X,F10.6)                                     FEL01010
C                                                                     FEL01020
C----- DIMENSIONLESS TIME                                           FEL01030
C                                                                     FEL01040
      DO 4 IT=1,ITMAX                                                 FEL01050
      DTT(IT)=DCO*60.*DTT(IT)/(0.25*THICK*THICK)                      FEL01060
    4 CONTINUE                                                        FEL01070
```

```
C                                                                       FEL01080
C ----                                                                  FEL01090
C                                                                       FEL01100
      ENEW=0.0                                                          FEL01110
      EENEW=0.0                                                         FEL01120
      IL=1                                                              FEL01130
      JL=1                                                              FEL01140
   10 CONTINUE                                                          FEL01150
C                                                                       FEL01160
C ---- CALCULATION OF CONCENTRATION PROFILE AND QI                      FEL01170
C                                                                       FEL01180
      CALL CONCTR (AP,AN,AS,BP,C,CO,QI,QEXP,E,X,                        FEL01190
     K                    ITMAX,DTMAX,DTT,A,B,VO,                      FEL01200
     K                    DX,JB,JE,JEP1,NJ,JD,MPD,                     FEL01210
     K                    EI,ICOPPR,IOFILE,IOUT,ICONPR,IPLOT,          FEL01220
     K                    INTLPM,IQIPR)                                FEL01230
C                                                                       FEL01240
C ---- MINIMIZING THE ERROR BY CHANGING A AND B                         FEL01250
C                                                                       FEL01260
      ENEW=EI                                                           FEL01270
      IF (IERPR.EQ.0) GO TO 17                                          FEL01280
      WRITE (IOFILE,15) IL,JL,ENEW,EENEW,A,B                            FEL01290
   15 FORMAT (/,15X,'IL=',I5,15X,'JL=',I5,/,                            FEL01300
     K        15X,'ENEW =',G15.7,5X,'EENEW=',G15.7,/,                  FEL01310
     K        15X,'A    =',G17.6,10X,'B    =',G17.6,/)                FEL01320
   17 CONTINUE                                                          FEL01330
      IF (IL.GE.ILMAX.OR.JL.GE.JLMAX) GO TO 120                         FEL01340
      IF (IL.EQ.1) GO TO 20                                             FEL01350
      GO TO 30                                                          FEL01360
   20 CONTINUE                                                          FEL01370
      IL=IL+1                                                           FEL01380
      DB=PDB*B                                                          FEL01390
      B=B+DB                                                            FEL01400
      DELTB=PDELTB*B                                                    FEL01410
      EOLD=ENEW                                                         FEL01420
      GO TO 10                                                          FEL01430
   30 CONTINUE                                                          FEL01440
      IF (ENEW.LE.EOLD) GO TO 40                                        FEL01450
      GO TO 50                                                          FEL01460
   40 CONTINUE                                                          FEL01470
      IF (ABS(DB).GT.DELTB) GO TO 20                                    FEL01480
      GO TO 60                                                          FEL01490
   50 CONTINUE                                                          FEL01500
      DB=DB/2.                                                          FEL01510
      B=B-DB                                                            FEL01520
      GO TO 10                                                          FEL01530
   60 CONTINUE                                                          FEL01540
      EOLD=ENEW                                                         FEL01550
      EENEW=ENEW                                                        FEL01560
      IF (JL.EQ.1) GO TO 70                                             FEL01570
      GO TO 80                                                          FEL01580
```

```
 70 CONTINUE                                                        FEL01590
    JL=JL+1                                                         FEL01600
    DA=PDA*A                                                        FEL01610
    DELTA=PDELTA*A                                                  FEL01620
    A=A+DA                                                          FEL01630
    EEOLD=EENEW                                                     FEL01640
    GO TO  10                                                       FEL01650
 80 CONTINUE                                                        FEL01660
    IF (EENEW.LE.EEOLD) GO TO 90                                    FEL01670
    GO TO 100                                                       FEL01680
 90 IF (ABS(DA).GT.DELTA) GO TO 70                                  FEL01690
    GO TO 110                                                       FEL01700
100 CONTINUE                                                        FEL01710
    DA=DA/2.                                                        FEL01720
    A=A-DA                                                          FEL01730
    GO TO 10                                                        FEL01740
110 CONTINUE                                                        FEL01750
120 CONTINUE                                                        FEL01760
    IF (IPLOT.EQ.0) GO TO 500                                       FEL01770
    DO 300 IT=1,ITMAX                                               FEL01780
    WRITE (20,350) DTT(IT),QEXP(IT)                                 FEL01790
300 CONTINUE                                                        FEL01800
350 FORMAT (2X,2G14.7)                                              FEL01810
    DO 400 IT=1,ITMAX                                               FEL01820
    WRITE (21,350) DTT(IT),QI(IT)                                   FEL01830
400 CONTINUE                                                        FEL01840
500 CONTINUE                                                        FEL01850
    CLOSE (2)
    CLOSE ( 4 )
    CLOSE (20 )
    CLOSE (21 )
    CLOSE (30 )
    CLOSE (31 )
    CLOSE (32 )
    CLOSE (33 )
    CLOSE (34 )
    CLOSE (35 )
    CLOSE (36 )
    CLOSE (37 )
    CLOSE (38 )
    CLOSE (39 )
    CLOSE (40 )
    CLOSE (41 )
    CLOSE (42 )
    CLOSE (43 )
    STOP                                                            FEL01860
    END                                                             FEL01870
```

```
CCCC
```

```
    2 CONTINUE                                                              FEL02440
    3 INT=INT+1                                                             FEL02450
      DO 20 J=2,JE                                                          FEL02460
      Z=1.-VO*C(J)                                                          FEL02470
      ZZ=A+B*C(J)                                                           FEL02480
      Z1=Z*EXP(C(J)/ZZ)                                                     FEL02490
      Z2=0.25*(C(J+1)*C(J+1)-2.*C(J+1)*C(J-1)+C(J-1)*C(J-1))/ZZZ            FEL02500
      Z3=Z/ZZZ                                                              FEL02510
      Z4=Z1*Z2*A/(ZZ*ZZ)                                                    FEL02520
      AP(J)=(1.+DT*(Z4*VO+2.*Z1*Z3))                                        FEL02530
      ZZZZ=DT*Z1*Z3                                                         FEL02540
      AN(J)=ZZZZ                                                            FEL02550
      AS(J)=ZZZZ                                                            FEL02560
      BP(J)=DT*(Z4-2*Z1*Z2*VO)+CO(J)                                        FEL02570
   20 CONTINUE                                                              FEL02580
      Z=1.-VO*C(1)                                                          FEL02590
      ZZ=A+B*C(1)                                                           FEL02600
      Z5=DT*2.*Z*EXP(C(1)/ZZ)/ZZZ                                           FEL02610
      AP(1)=(1.+Z5)                                                         FEL02620
      AN(1)=Z5                                                              FEL02630
      AS(1)=0.                                                              FEL02640
      BP(1)=CO(1)                                                           FEL02650
      AP(JEP1)=1.0                                                          FEL02660
      AN(JEP1)=0.0                                                          FEL02670
      AS(JEP1)=0.0                                                          FEL02680
      BP(JEP1)=0.0                                                          FEL02690
C                                                                           FEL02700
C ---- PRINT THE COEFFICIENTS FOR THE SYSTEM OF EQUATION                    FEL02710
C                                                                           FEL02720
      IF (ICOFPR.EQ.0) GO TO 45                                             FEL02730
      DO 30 J=1,JD                                                          FEL02740
      WRITE (IOFILE,40) AP(J),AN(J),AS(J),BP(J)                             FEL02750
   30 CONTINUE                                                              FEL02760
   40 FORMAT (5X,4(G14.5,3X))                                               FEL02770
   45 CONTINUE                                                              FEL02780
C                                                                           FEL02790
C---- THE SOLUTION FOR THE SYSTEM OF EQAUTIONS                              FEL02800
C----- TDMA FORTRAN                                                         FEL02830
C                                                                           FEL02840
      CALL FACTR1(C,AP,AN,AS,BP,JB,JE,JD)                                   FEL02850
C                                                                           FEL02860
C---- SWEEP                                                                 FEL02870
      IF (INT.LE.INTLPM) GO TO 3                                            FEL02900
C                                                                           FEL02910
C----- PRINTTTHE CONCENTRATION PROFILE                                      FEL02920
C                                                                           FEL02930
      IF (ICONPR.EQ.0) GO TO 80                                             FEL02940
      IF (IKOUNT.EQ.IDT) GO TO 50                                           FEL02950
      GO TO 80                                                              FEL02960
   50 CONTINUE                                                              FEL02970
      WRITE (IOUT,70) T,(C(J),J=1,11)                                       FEL02980
 70   FORMAT(/,6X,E10.3,//,15X,4(E11.4,3X),/,15X,4(E11.4,3X),/,15X,3(       FEL02990
     X E11.4,3X))                                                           FEL03000
   80 CONTINUE                                                              FEL03010
```

```
C                                                                       FEL03020
C----- PLOT THE CONCENTRATION PROFILE                                   FEL03030
C                                                                       FEL03040
      IF (IPLOT.EQ.0) GO TO 300                                         FEL03050
      IF (IKOUNT.EQ.IDT) GO TO 310                                      FEL03060
      GO TO 300                                                         FEL03070
  310 CONTINUE                                                          FEL03080
      IFILE=IFILE+1.                                                    FEL03090
      DO 320 J=1,NJ                                                     FEL03100
      WRITE (IFILE,330) X(J),C(J)                                       FEL03110
  320 CONTINUE                                                          FEL03120
  330 FORMAT (2X,2(G14.7,1X))                                           FEL03130
  300 CONTINUE                                                          FEL03140
      IF (C(JB).GT.10) GO TO 140                                        FEL03150
      IF (IKOUNT.LT.IDT) GO TO 1                                        FEL03160
C                                                                       FEL03170
C ---- CALCULATION OF THE QI USING SIMPSON'S RULE                       FEL03180
C                                                                       FEL03190
      DI=0.0                                                            FEL03200
      DO 90 J=JB,JE,2                                                   FEL03210
      DI=DI+(DX/3.)*(C(J-1)+4.*C(J)+C(J+1))                             FEL03220
   90 CONTINUE                                                          FEL03230
      QI(IT)=DI                                                         FEL03240
      IF (IQIPR.EQ.0) GO TO 125                                         FEL03250
      WRITE (IOFILE,123) DTT(IT),QEXP(IT),T,QI(IT)                      FEL03260
  123 FORMAT (6X,4(G15.7,5X))                                           FEL03270
  125 CONTINUE                                                          FEL03280
C                                                                       FEL03290
100   CONTINUE                                                          FEL03300
C                                                                       FEL03310
C ---- ERROR CALCULATION USING SIMPSON'S RULE FOR NONUNIFORM INTERVAL   FEL03320
C                                                                       FEL03330
      DO 120 I=1,ITMAX                                                  FEL03340
      EE=QEXP(I)-QI(I)                                                  FEL03350
      E(I)=EE*EE                                                        FEL03360
  120 CONTINUE                                                          FEL03370
      ITM1=ITMAX-1                                                      FEL03380
      DI=0.0                                                            FEL03390
      DO 130 I=2,ITM1,2                                                 FEL03400
      DTM=DTT(I)-DTT(I-1)                                               FEL03410
      DTP=DTT(I+1)-DTT(I)                                               FEL03420
      F=1./DTM                                                          FEL03430
      FF=1./DTP                                                         FEL03440
      G=DTM+DTP                                                         FEL03450
      GG=DTP*DTP-DTM*DTM                                                FEL03460
      GGG=DTP*DTP*DTP+DTM*DTM*DTM                                       FEL03470
      DI=DI+(GGG*F/(3.*G)-GG*F*DTP/(2.*G))*E(I-1)                       FEL03480
     K      +(G+(GG*(FF*DTM-F*DTP))/(2.*G)-(GGG*(F+FF))/(3.*G))*E(I)    FEL03490
     K      +(GG*DTM*FF/(2.*G)+GGG*FF/(3.*G))*E(I+1)                    FEL03500
  130 CONTINUE                                                          FEL03510
      EI=DI                                                             FEL03520
  140 CONTINUE                                                          FEL03530
      RETURN                                                            FEL03540
      END                                                               FEL03550
```

```
C                                                                       FEL03590
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC FEL03600
C      TDMA FORTRAN                                                     FEL03610
      SUBROUTINE FACTR1(T,AP,AN,AS,BP,JB,JE,JD)                         FEL03620
C                                                                       FEL03630
C     SUBROUTINE TO OBTAIN OR UPDATE SOLUTION OF A SET OF THREE POINT   FEL03640
C     ALGEBRAIC EQUATIONS USING THE TDMA ALGORITHM                      FEL03650
C                                                                       FEL03660
C     TWO STAGE PROCESS; CALL FACTR1-TO SET RECURSIVE RELATIONS         FEL03670
C                                 FOR A GIVEN SET OF A-COEF'S           FEL03680
C                        CALL SWEEP1-TO APPLY THE TDMA .NOTE THAT       FEL03690
C                                 B MAY CHANGE WITHOUT HAVING           FEL03700
C                                 TO RECOMPUTE THE RECURSIVE            FEL03710
C                                 RELATIONS.                            FEL03720
C                                                                       FEL03730
C     T(J)= DEPENDENT FIELD VARIABLE                                    FEL03740
C     AP(J),AN(J),AS(J)= A-COEFICIENTS                                  FEL03750
C     BP(J)= 'SOURCE' TERM COEFICIENTS                                  FEL03760
C     JB,JE= BEGINNING AND ENDING INDEX VALUES FOR Y DIRECTION          FEL03770
C              NOTE; JB AND JE CORRESPOND TO LIMITS OF INDICES FOR      FEL03780
C                    INTERIOR OF DOMAIN. JB MUST BE >1                  FEL03790
C     JD= DIMENSION OF ALL ARRAYS IN ARGUMENT LIST. JD < 101            FEL03800
C                                                                       FEL03810
C     THE ALGEBRAIC EQUATIONS HAVE THE FORM:                            FEL03820
C      AP(J)*T(J)=AN(J)*T(J+1)+AS(J)*T(J-1)+BP(J)                       FEL03830
C                                                                       FEL03840
C     THE RECURRSIVE RELATIONS HAVE THE FORM:                           FEL03850
C      T(J)=(AN(J)*T(J+1)+F(J))/E(J)                                    FEL03860
C                                                                       FEL03870
C     BOUNDARY CONDITIONS ARE ASSUMED SUPPLIED IN COEFICIENTS IN        FEL03880
C     JB-1 AND JE+1 LOCATIONS                                           FEL03890
C                                                                       FEL03900
C                                                                       FEL03910
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC FEL03920
      REAL T(JD),AP(JD),AN(JD),AS(JD),BP(JD)                            FEL03930
      REAL E(100),F(100)                                                FEL03940
      JBM1=JB-1                                                         FEL03950
      JEP1=JE+1                                                         FEL03960
      E(JBM1)=AP(JBM1)                                                  FEL03970
      DO 10 J=JB,JEP1                                                   FEL03980
      E(J)=AP(J)-AS(J)*AN(J-1)/E(J-1)                                   FEL03990
   10 CONTINUE                                                          FEL04000
      F(JBM1)=BP(JBM1)                                                  FEL04030
      DO 20 J=JB,JEP1                                                   FEL04040
      F(J)=BP(J)+AS(J)*F(J-1)/E(J-1)                                    FEL04050
   20 CONTINUE                                                          FEL04060
      T(JEP1)=F(JEP1)/E(JEP1)                                           FEL04070
      DO 30 JJ=JBM1,JE                                                  FEL04080
      J=JE-JJ+JBM1                                                      FEL04090
      T(J)=(AN(J)*T(J+1)+F(J))/E(J)                                     FEL04100
   30 CONTINUE                                                          FEL04110
      RETURN                                                            FEL04120
      END                                                               FEL04130
```

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Theoretical Concentration-Time Profile for the Bis(2-Chloroethyl) Sulphide-Natural Rubber System

TBAR	CBAR AT POSITION OF C			
.000E+00				
	.1000E+01	.1000E+01	.1000E+01	.1000E+01
	.1000E+01	.1000E+01	.1000E+01	.1000E+01
	.1000E+01	.1000E+01	.1000E+01	
.660E-02				
	.9977E+00	.9976E+00	.9971E+00	.9952E+00
	.9900E+00	.9779E+00	.9527E+00	.9021E+00
	.8000E+00	.5785E+00	.0000E+00	
.165E-01				
	.8277E+00	.8257E+00	.8184E+00	.8056E+00
	.7866E+00	.7607E+00	.7270E+00	.6841E+00
	.6300E+00	.5500E+00	.0000E+00	
.231E-01				
	.7446E+00	.7423E+00	.7344E+00	.7204E+00
	.6996E+00	.6709E+00	.6323E+00	.5804E+00
	.5089E+00	.4044E+00	.0000E+00	
.297E-01				
	.6761E+00	.6738E+00	.6659E+00	.6521E+00
	.6317E+00	.6036E+00	.5662E+00	.5162E+00
	.4475E+00	.3439E+00	.0000E+00	
.396E-01				
	.5989E+00	.5966E+00	.5890E+00	.5757E+00
	.5562E+00	.5296E+00	.4943E+00	.4476E+00
	.3838E+00	.2881E+00	.0000E+00	
.462E-01				
	.5568E+00	.5547E+00	.5475E+00	.5349E+00
	.5165E+00	.4912E+00	.4575E+00	.4123E+00
	.3498E+00	.2547E+00	.0000E+00	
.561E-01				
	.5065E+00	.5044E+00	.4975E+00	.4856E+00
	.4680E+00	.4438E+00	.4117E+00	.3689E+00
	.3101E+00	.2214E+00	.0000E+00	

.627E-01

.4776E+00	.4756E+00	.4690E+00	.4576E+00
.4407E+00	.4175E+00	.3866E+00	.3452E+00
.2879E+00	.2011E+00	.0000E+00	

.693E-01

.4522E+00	.4503E+00	.4440E+00	.4329E+00
.4166E+00	.3942E+00	.3642E+00	.3240E+00
.2685E+00	.1847E+00	.0000E+00	

.759E-01

.4297E+00	.4278E+00	.4217E+00	.4109E+00
.3951E+00	.3733E+00	.3442E+00	.3053E+00
.2515E+00	.1707E+00	.0000E+00	

.825E-01

.4095E+00	.4076E+00	.4016E+00	.3912E+00
.3758E+00	.3546E+00	.3263E+00	.2885E+00
.2363E+00	.1585E+00	.0000E+00	

.891E-01

.3911E+00	.3894E+00	.3835E+00	.3733E+00
.3583E+00	.3377E+00	.3101E+00	.2733E+00
.2227E+00	.1477E+00	.0000E+00	

.957E-01

.3744E+00	.3727E+00	.3670E+00	.3570E+00
.3424E+00	.3223E+00	.2954E+00	.2596E+00
.2105E+00	.1380E+00	.0000E+00	

.102E+00

.3591E+00	.3574E+00	.3518E+00	.3421E+00
.3278E+00	.3081E+00	.2819E+00	.2470E+00
.1994E+00	.1294E+00	.0000E+00	

.109E+00

.3450E+00	.3433E+00	.3378E+00	.3283E+00
.3143E+00	.2951E+00	.2696E+00	.2355E+00
.1892E+00	.1217E+00	.0000E+00	

.116E+00

.3319E+00	.3303E+00	.3249E+00	.3156E+00
.3019E+00	.2831E+00	.2581E+00	.2249E+00
.1799E+00	.1147E+00	.0000E+00	

.127E+00

.3111E+00	.3095E+00	.3043E+00	.2953E+00
.2821E+00	.2641E+00	.2401E+00	.2083E+00
.1653E+00	.1038E+00	.0000E+00	

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TBAR	CBAR AT POSITION OF C			
.000E+00				
	.1000E+01	.1000E+01	.1000E+01	.1000E+01
	.1000E+01	.1000E+01	.1000E+01	.1000E+01
	.1000E+01	.1000E+01	.1000E+01	
.176E-01				
	.9672E+00	.9656E+00	.9590E+00	.9466E+00
	.9263E+00	.8946E+00	.8459E+00	.7709E+00
	.6536E+00	.4613E+00	.0000E+00	
.353E-01				
	.8896E+00	.8866E+00	.8752E+00	.8547E+00
	.8236E+00	.7794E+00	.7185E+00	.6348E+00
	.5175E+00	.3418E+00	.0000E+00	
.529E-01				
	.8099E+00	.8065E+00	.7941E+00	.7722E+00
	.7395E+00	.6942E+00	.6335E+00	.5523E+00
	.4416E+00	.2814E+00	.0000E+00	
.661E-01				
	.7554E+00	.7520E+00	.7396E+00	.7179E+00
	.6858E+00	.6416E+00	.5827E+00	.5046E+00
	.3992E+00	.2492E+00	.0000E+00	
.838E-01				
	.6918E+00	.6884E+00	.6764E+00	.6554E+00
	.6245E+00	.5822E+00	.5261E+00	.4523E+00
	.3541E+00	.2170E+00	.0000E+00	
.101E+00				
	.6366E+00	.6333E+00	.6218E+00	.6016E+00
	.5720E+00	.5317E+00	.4784E+00	.4089E+00
	.3171E+00	.1911E+00	.0000E+00	
.123E+00				
	.5768E+00	.5736E+00	.5627E+00	.5437E+00
	.5158E+00	.4778E+00	.4280E+00	.3633E+00
	.2788E+00	.1649E+00	.0000E+00	

.141E+00

.5355E+00 .5324E+00 .5219E+00 .5037E+00
.4770E+00 .4408E+00 .3934E+00 .3323E+00
.2531E+00 .1480E+00 .0000E+00

.159E+00

.4986E+00 .4956E+00 .4856E+00 .4681E+00
.4425E+00 .4080E+00 .3630E+00 .3052E+00
.2308E+00 .1335E+00 .0000E+00

.176E+00

.4655E+00 .4626E+00 .4529E+00 .4361E+00
.4117E+00 .3787E+00 .3359E+00 .2812E+00
.2114E+00 .1210E+00 .0000E+00

.194E+00

.4356E+00 .4328E+00 .4235E+00 .4074E+00
.3840E+00 .3525E+00 .3117E+00 .2598E+00
.1942E+00 .1102E+00 .0000E+00

.212E+00

.4084E+00 .4057E+00 .3967E+00 .3813E+00
.3588E+00 .3287E+00 .2899E+00 .2407E+00
.1789E+00 .1007E+00 .0000E+00

.229E+00

.3836E+00 .3810E+00 .3723E+00 .3575E+00
.3360E+00 .3072E+00 .2702E+00 .2235E+00
.1653E+00 .9240E-01 .0000E+00

.234E+00

.3777E+00 .3751E+00 .3665E+00 .3518E+00
.3305E+00 .3021E+00 .2655E+00 .2195E+00
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